THE JOURNAL
OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

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IMPORT - EXPORT

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give plumper, tighter, brighter

WHITE LEATHER

ZIRCOTAN S / LEUKANOL C

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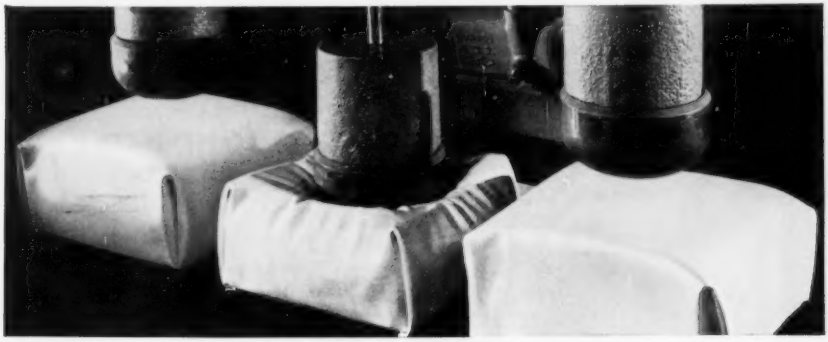

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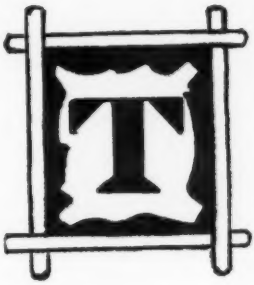

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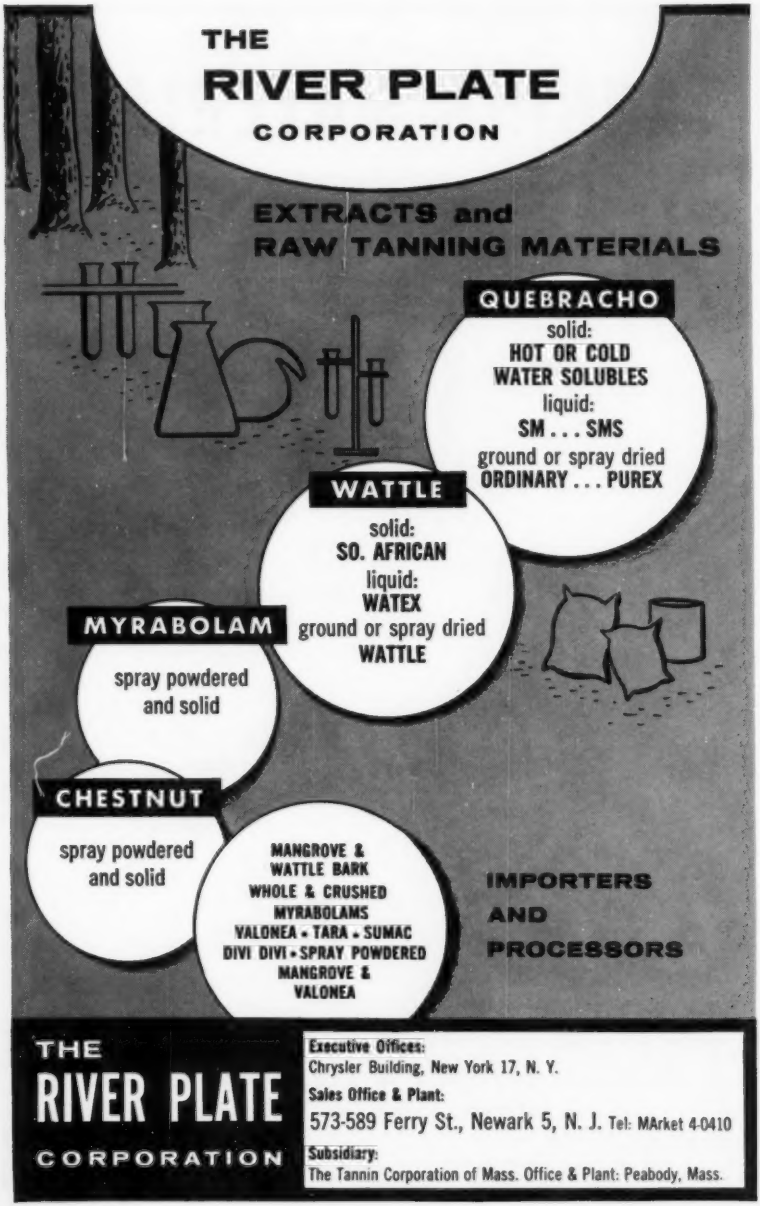
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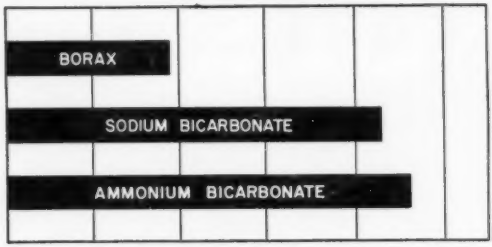
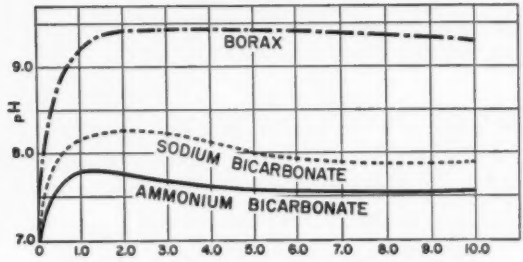


Pounds of hydrochloric acid neutralized by 1 lb. of alkali

at Lower pH for



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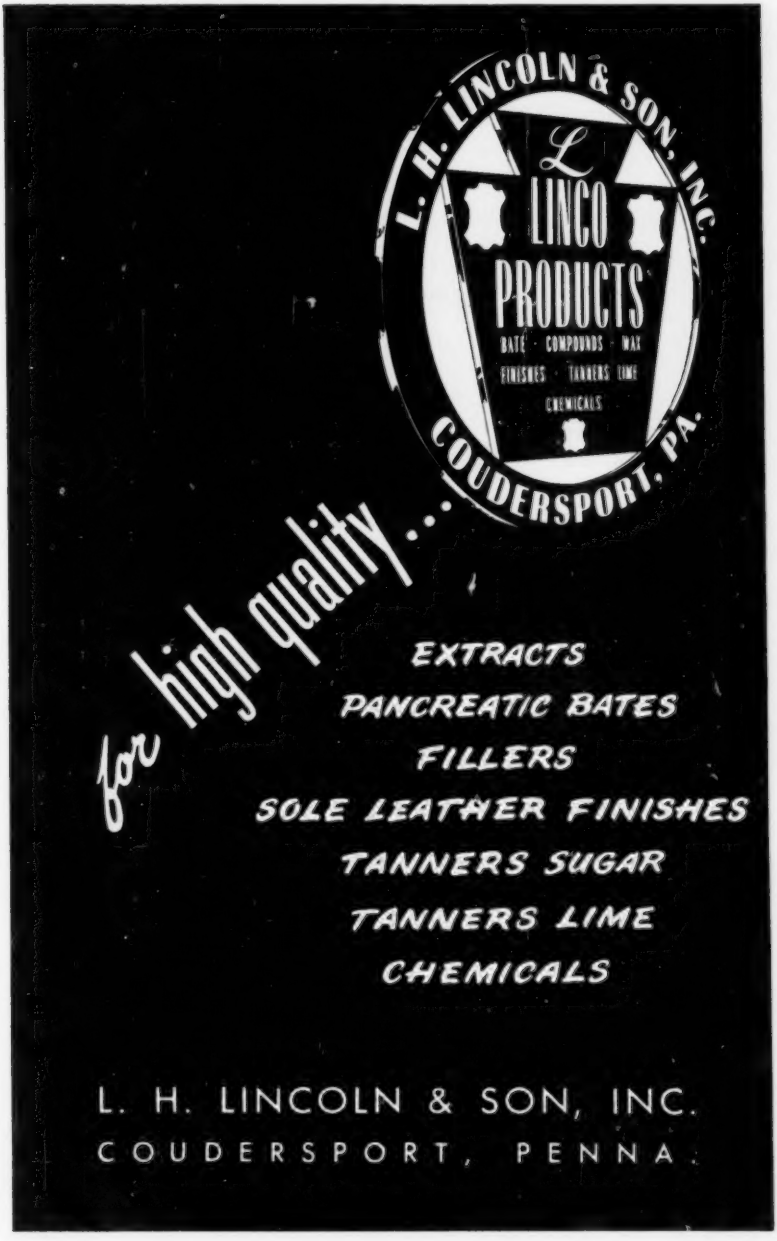
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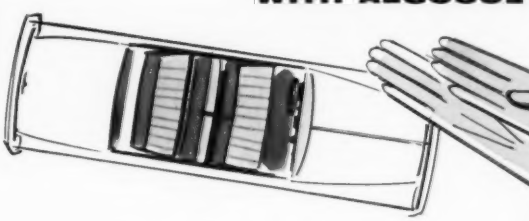

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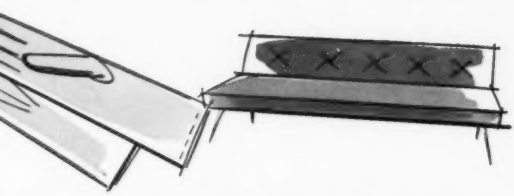

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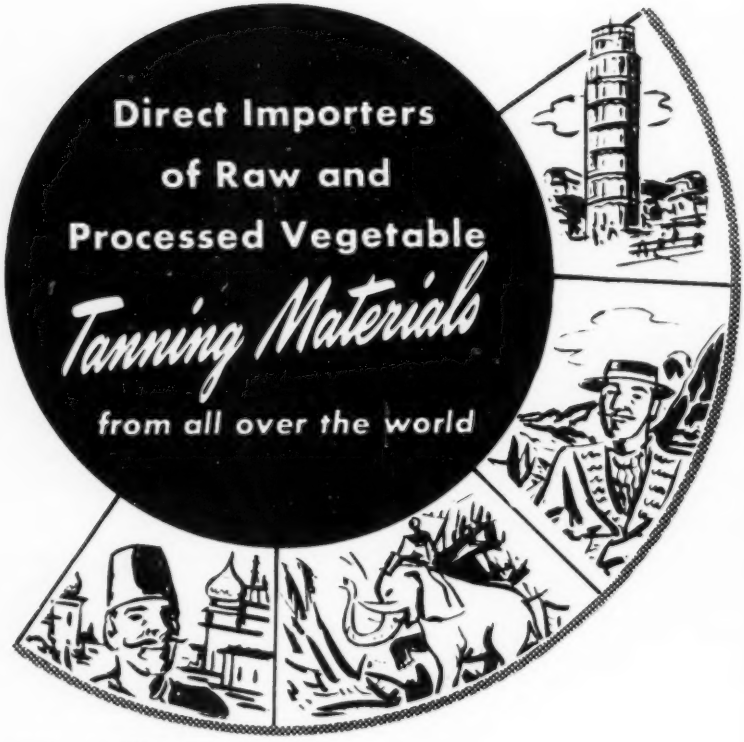

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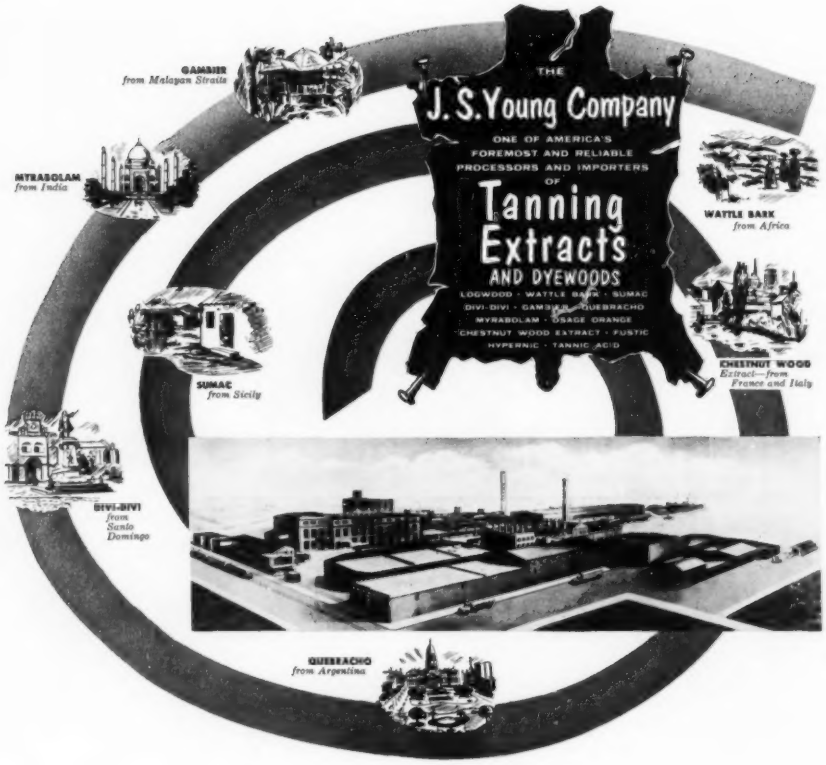

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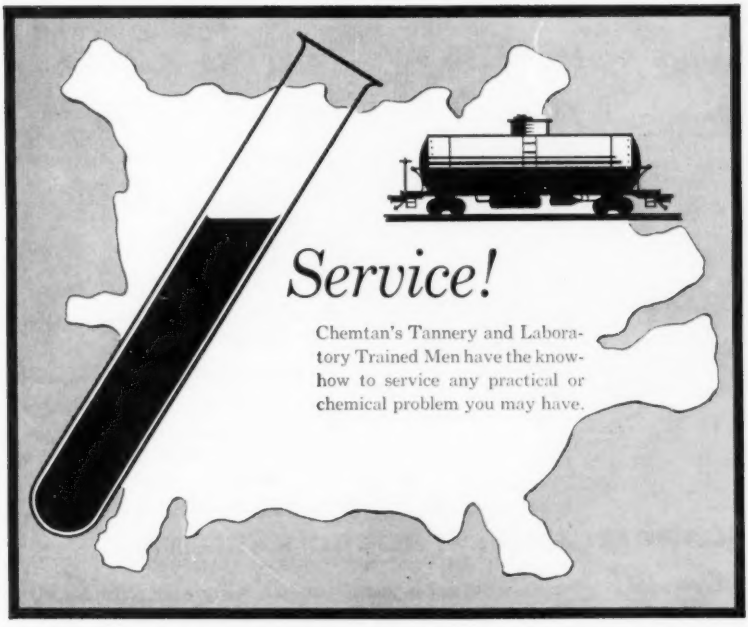
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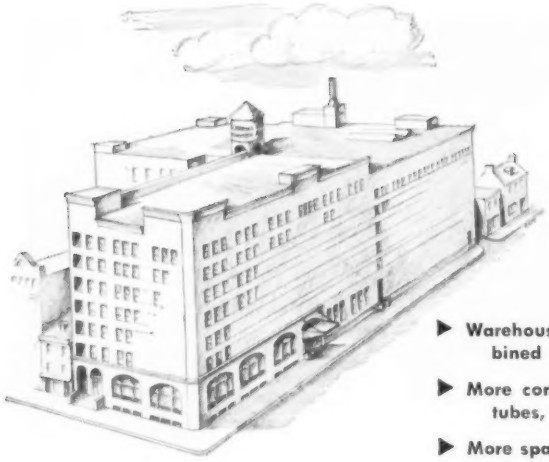

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NEW DEVELOPMENTS IN TANNING WITH ALDEHYDES*

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ABSTRACT

A comprehensive study of the tanning action of aliphatic dialdehydes with straight carbon-carbon chains was initiated.

The lowest member, glyoxal, was found to have the best tanning properties, ranking close to formaldehyde when employed at its optimum pH range, which is between 9 and 10. Both aldehydes produce a smooth-grained, strong, and relatively soft leather when this pH range is maintained by the use of fairly concentrated alkaline solutions, preferably 2 *N* sodium carbonate or mixtures of sodium carbonate and bicarbonate with similar normalities.

The next two members of the series, malonaldehyde and succinaldehyde, tan best in the acid range, notably between pH 3.5 and 4.5. They tan less well at pH 7 or in the alkaline range. The tanning properties of succinaldehyde surpass those of malonaldehyde under all experimental conditions tested so far.

Glutaraldehyde is a good tanning agent over a very wide pH range, but α-hydroxyadipaldehyde is, evidently for steric reasons, a particularly weak tanning agent.

INTRODUCTION

From the point of view of tanning theory, investigations of the reaction between collagen and formaldehyde have proved particularly fruitful. That aliphatic dialdehydes should likewise be of great interest was pointed out by the senior author (1) in 1941, but it was six years later before the tanning action of even the simplest dialdehyde, glyoxal, was investigated (2). Other dialdehydes have become available in recent years without arousing much interest despite their potentialities as tanning agents. These aldehydes, however, form a class of domestic tanning materials which can be supplied by our chemical industry in practically unlimited quantities. This was sufficient reason for the Quartermaster Research and Development Command to explore their possible usefulness in tannery practice. The results have been gratifying in two respects: A new and practical tanning method, using inexpensive aldehydes like formaldehyde and glyoxal, was developed, and unexpectedly good tanning effects were obtained with the three dialdehydes possessing straight chains of 3, 4, and 5 carbon atoms. All these tannages, moreover, open new possibilities of preparing leather for subsequent treatment with vegetable extracts or their substitutes and replacement materials. A report on these combination tannages in a separate paper is contemplated. The present study will deal principally with the aldehyde tannages themselves and will show the striking differences existing within the dialdehyde series.

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EXPERIMENTAL

Tanning Methods.—Cowhide obtained from a tannery in the pickled state was used for all experiments except one. This pickled stock included heavy bends, sides, and grain splits for garment leather. For tanning, the stock was cut in rectangular or square pieces of varying sizes. A large number of tests were conducted with squares, randomized by using Latin square designs.

The tanning experiments were conducted over a wide pH range. Alkaline solutions were adjusted to a desired normality; in so doing, the water carried over by the stock itself was taken into account. The volume of these solutions was calculated on the basis of the drained pickled weight, in accordance with tannery practice.

The test pieces were tumbled in glass jars for several hours with the alkaline liquor, and after a night's rest, for at least five hours with the tanning agent. The next day the tanned pieces were transferred to a salt solution in which they were neutralized by the gradual addition of mineral acid and/or acetic acid. After the equilibrium pH of the leather pieces had dropped to between 5 and 6, they were given a good wash in a photographic print-washer, and hung up to dry at room temperature or in mild heat.

For experiments in the acid pH range, the test pieces were tumbled in the presence of a dilute NaCl solution, to which in many instances a small quantity of H_2SO_4 was added in order to lower the pH to the desired level. After the tanning agent had struck through, the pH of the test pieces was gradually raised by feeding $NaHCO_3$ or Na_2CO_3.

Examination of Leathers.—Formaldehyde in leathers was determined by the method of Highberger and Retszch (5*a*), modified slightly to improve the finality of the end point. Instead of adding ethanol and 5% Na_2CO_3 solution to the iodine solution, we added 15 ml. of saturated $NaHCO_3$, followed by 1 or 2 ml. of 2 *N* Na_2CO_3 toward the very end of the titration, as recommended by Friedemann and Graeser (7). Formaldehyde was determined in duplicate on the leather in the air-dry condition as well as after weighing the loss incurred by drying. On the average, 9.2% of the total formaldehyde was given up by the leather while drying. Formula I below was used for computing hide substance, and Formula II was used for calculating formaldehyde, using charges of exactly 1 g. of leather for the latter.

$$\text{I.}\quad \%\ \text{hide substance (dry basis)} = \frac{A_1\ N_1 \times 7.87}{W_1 \times [100\ W_2 + 15N_2(A_2-A_3)]}$$

$$\text{II.}\quad \%\ \text{formaldehyde (dry basis)} = \frac{A_2\ N_2 \times 1.5}{100\ W_2 + 15\ N_2\ (A_2-A_3)}$$

where A_1 = ml. of H_2SO_4 of normality N_1 for titrating hide substance,

A_2=ml. of iodine solution of normality N_2 for titrating formaldehyde in the air-dry charge,

A_3=ml. of iodine solution of normality N_2 for titrating formaldehyde in the oven-dried charge,

W_1=g. of air-dry leather for determination of hide substance, and

W_2=g. weight of 1 g. air-dry leather after drying 16 hours at 100°C.

Since no methods exist for the direct determination of glyoxal and higher aldehydes, these were estimated by determining hide substance, fat, moisture, and ash by the methods of Federal Specification KK-L-331a, and subtracting their sum from 100. This procedure was applied also to the formaldehyde leathers. As will be seen later (Table V) the difference between 100 and the sum of hide substance, fat, and ash (on the dry basis) is always less than the percentage of formaldehyde determined directly. The sum of the other constituents may even exceed 100%. The existence of cross-linkages appears to explain only a part of this discrepancy. A satisfactory explanation may, we hope, be found in the course of future work. This discrepancy between results obtained by the direct and indirect determinations of formaldehyde of course casts doubt on the accuracy of the indirect determination of the dialdehyde. It is of interest that no dialdehyde-tanned leather reacted positively to Schiff's reagent, although the fresh solutions of the dialdehydes invariably do so.

The leathers were tested for shrinkage temperature (T_s), pH, presence of aldehyde (qualitative test), and elongation at break by the methods of Federal Specification KK-L-311a, except that a specimen 4" long and 0.25" wide at the "waist" was used for the elongation test, because of the smallness of the experimental leather squares. Bursting strength was measured with a $\frac{1}{8}$-inch plunger (6).

RESULTS

Formaldehyde and Glyoxal.—Among the first tanning experiments carried out in the alkaline medium was a series with glyoxal, recorded in Table I. In all but one instance, NaOH was used either alone or in combination with Na_2CO_3 or Na_2SO_4. The exception was a test employing 2 *N* Na_2CO_3. Here, as may be observed in Table I, the T_s rose to 87°C., which is much higher than any T_s previously reported for glyoxal tannage. When NaOH was present, alone or as part of the alkaline system, tanning was prevented, except for the 1 *N* NaOH/Na_2SO_4 system which supported a moderate tannage.

Measurements of thickness and strength on those pieces that showed evidence of a tanning action revealed that the leather tanned in the NaOH/Na_2SO_4 system is only half as thick as that tanned in 2 *N* Na_2CO_3 solutions and that both types of leather possess the same bursting strength in pounds;

therefore the depressed and flaccid leather is about twice as strong on the same thickness basis.

TABLE I

GLYOXAL TANNAGE IN ALKALINE SOLUTIONS

LATIN SQUARE TEST NO. 1

(*Pickled cow grains for garment tanned in* 100 *volume per cent, on drained pickled weight*)

Latin Square Letters	(a)	(b)	(c)	(d)	(e)
Normality of Na_2CO_3	2.0	2.0	—	—	—
Normality of NaOH	—	1.0	1.0	1.0	2.0
Normality of Na_2SO_4	—	—	—	1.0	1.0
pH after glyoxal tan (next A.M.)	9.4	11.8	11.9	11.5	11.6
Ts after glyoxal tan, °C.	87	60	50	71	49
pH after neutralization	5.4	5.3	5.4	5.6	5.0
Thickness, inches	0.110	—	—	0.053	—
Bursting strength, lb.	50	—	—	52	—
Bursting strength, lb/in	460	—	—	985	—

In the experiments shown in Table II the hide pieces were first brought to equilibrium with a solution containing 2 moles $NaHCO_3$ for every mole Na_2CO_3. The solutions were either 2 *N* or 0.5 *N* depending on the "float" (40% or 400% on the drained pickled weight). Formaldehyde and glyoxal were employed as tanning agents at both levels of concentration, and the results obtained are strikingly similar. Both tannages produce stronger leather in more concentrated solutions, bursting strength being about 30% and breaking force at least 70% greater than in the dilute solutions. The increase in elongation at break is more moderate but also very distinct.

A number of experiments were made for the purpose of comparing neutralization and washing with running water. In one test, pieces from a double bend were tanned with glyoxal. The bursting strength of the neutralized piece averaged 985 lb/in, and that of the washed piece 848 lb/in, i.e., 14% less.

In the next experiment on the effect of washing, pieces of glyoxal-tanned cow grain leather were washed or neutralized. Here the loss of bursting strength for the washed pieces is about 25%. As Table III shows, this experiment included two more sets of hide pieces tanned in 0.5 *N* alkaline solutions, one set with glyoxal and one with formaldehyde. All tannages were conducted with a 400% float. Both aldehydes in 0.5 *N* alkaline solutions produce leathers of equal strength, but this strength is nearly 60% below that obtained with glyoxal at the higher level of alkalinity. This difference is

TABLE II

ALDEHYDE TANNAGE IN ALKALINE SOLUTIONS

LATIN SQUARE TEST NO. 2

(Pickled sides for shoe upper leather)

Latin Square Letters Aldehyde	(a) Glyoxal	(b) Formaldehyde	(c) Glyoxal	(d) Formaldehyde
TANNING CONDITIONS				
Normality of Na_2CO_3, calculated	0.25	0.25	1.0	1.0
Normality of $NaHCO_3$, calculated	0.25	0.25	1.0	1.0
% Na_2CO_3 (approx.)*	6.25	6.25	5.88	5.88
% $NaHCO_3$ (approx.)*	10	10	9.25	9.25
Volume of tan liquor, %*	400	400	40	40
Ts, °C., at end of tan	87	88	86	90
pH at end of tan	9.0	——	9.0	8.8
% H_2SO_4 used for neutralization*	2.5	2.6	3.7†	4.8
PHYSICAL PROPERTIES				
Thickness, inches‡	0.140	0.157	0.123	0.111
Bursting strength, lb.	87	84	110	112
Bursting strength, lb/in	630	520	895	965
Breaking force, lb.	36	31	61	57
Tensile strength, lb/in	1020	816	2000	2115
Ratio of bursting to breaking strength	0.62	0.64	0.45	0.46
Increase in bursting strength			27% over (a)	34% over (b)
Increase in breaking strength			70% over (a)	84% over (b)
Condition of grain	raspy and tender	raspy and tender	smooth and pliable	smooth and pliable

*On drained, pickled weight.
†Less than for (d) because of partial conversion of glyoxal to glycolic acid.
‡Average of all measurements made in determining tensile strength and bursting strength.

about double that observed in Test No. 1 (Table I) on a hide which was three times thicker.

Tanning in a large float is, of course, uneconomical and unnecessary when soda and bicarbonate concentrations of the desired magnitude are required. For example, the 2 *N* soda solution recorded in Table III requires 50%, and the 0.5 *N* solution, 12.5%, soda ash, both on the drained pickled weight. Hence, under practical tanning conditions, a short float is certainly imperative with alkaline solutions of 1.5 *N* and above.

The effect of pickling on tanning with formaldehyde and glyoxal was investigated in the next experiment. Pieces of bated cowhide were cut in half, and one group of half-pieces was given an acid pickle, which lowered the pH

to approximately 2.0. Both pickled and bated pieces were tanned in a 2 *N* Na_2CO_3 solution. The results of these treatments, presented in Table IV, show that pickling increases the bursting strength by more than 20%.

TABLE III

ALDEHYDE TANNAGE IN ALKALINE SOLUTIONS

LATIN SQUARE TEST NO. 3

(*Pickled cow grains for garment, tanned in 400 volume per cent float on drained pickled weight*)

Latin Square Letters Aldehyde	(a) Glyoxal	(b) Glyoxal	(c) Glyoxal	(d) Formal-dehyde
TANNING CONDITIONS				
Normality of Na_2CO_3	2.0	0.5	2.0	0.5
Ts, °C., at end of tan	86	87	86	89
pH at end of tan	—	9.9	—	10.2
% H_2SO_4 required for neutralization*	3.0	2.0	washed	2.2
% acetic acid (used with H_2SO_4 for neutralization)*	2.0	2.0		2.0
PHYSICAL PROPERTIES				
1. Thickness, inches	0.036	0.049	0.046	0.050
2. Bursting strength, lb	25	14	19	13
3. Bursting strength, lb/in	695	285	455	260

*On drained pickled weight.

TABLE IV

ALDEHYDE TANNAGE IN SODIUM CARBONATE SOLUTIONS ON BATED AND PICKLED COWHIDE

(1.8% *pure aldehyde on bated weight*)

	Formaldehyde		Glyoxal	
	Unpickled	Pickled	Unpickled	Pickled
pH of resulting leather	7.0	7.2	5.9	5.9
Ts, °C.	83	84	87	85
% fixed aldehyde, of hide substance	2.3	2.0	3.2	3.9
Thickness, inches	0.13	0.13	0.18	0.19
Bursting strength, lb.	87	105	135	170
% increase in bursting strength by pickle treatment		21		26

Malonaldehyde and Succinaldehyde.—Acetals, which produce these aldehydes on hydrolysis, have recently become commercially available. Such acetals are very convenient sources of aldehydes for tanning because they are easily hydrolyzed by the pickle acid in hides or skins.

For setting up tanning experiments it is important to know how much aldehyde, at least in theory, can be obtained from the various acetals. The yields, as well as the equations on which these yields are based, are as follows:

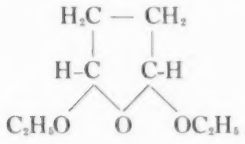
Tetra-alkoxypropane

$$(RO)_2CHCH_2CH(OR)_2 + 2\ H_2O = OCH(CH_2)CHO + 4\ ROH$$

When R $= CH_3$, molecular weight $= 164.2$
Yield of malonaldehyde $= 43.9\%$

When R $= C_2H_5$, molecular weight $= 220.3$
Yield of malonaldehyde $= 32.7\%$

Diethyltetrahydrofuran



$$+ H_2O = OCH(CH_2)_2CHO + 2\ C_2H_5OH$$

Molecular weight $= 160.2$
Yield of succinaldehyde $= 53.7\%$

The rates of hydrolysis for alkoxypropanes depend on their solubilities in water. For example, 100 parts of a saturated aqueous solution contains 32 parts of the symmetrical methoxypropane, compared with 1.8 parts of the symmetrical ethoxypropane and 3.6 parts of a mixed alkoxypropane with 1 ethoxy and 3 methoxy groups (3). In a very striking experiment 5 ml. of the wholly methoxylated acetal were shaken for about 1.5 hours with only 1 ml. of a 0.25 *N* H_2SO_4 solution, then diluted with 4 ml. water and shaken again for 0.5 hour. A clear solution was obtained. The other two acetals did not hydrolyze with the same volume of acid, unless shaken for many hours before as well as after dilution with water.

Succinaldehyde, obtained by hydrolyzing its acetal with sulfuric acid, is relatively stable as indicated by the fact that its solutions may be brought to pH 5 and then aged or boiled without impairing its tanning action. However, malonaldehyde decomposes fairly rapidly, even in the cold, turning dark brown on standing. It cannot be boiled or aged without losing its tanning properties as the decomposition products formed under these conditions are not tanning agents.

In order to find the optimum pH for tanning with malonaldehyde and succinaldehyde, several experiments were run with depickled hide. The acetals were hydrolyzed with dilute acid and the aqueous solutions neutralized by careful addition of caustic soda. The pH of hide and liquor, initially around 7.5, was lowered gradually by additions of dilute mineral acid, and as the pH of the solution dropped, a slow rise of T_s was noted. A maximum T_s was reached in the pH range between 3 and 4.5. Below pH 3 a sharp decline in T_s was observed.

In the next experiment calcium carbonate was employed to maintain the pH above 7 at the outset of tanning experiments with the two aldehydes. Malonaldehyde, after three days, produced a T_s of only 61°C. After lowering the pH to 3.9, the T_s rose within two days to 74°C. and in another three days to 78°C. Succinaldehyde, on the other hand, did exercise a distinct tanning action around pH 7, marked by a T_s of 70°C. Upon lowering the pH, however, the T_s rose to 73°C. within a few hours and to 76.5°C. the next day.

These findings show that Winheim and Doherty (*4a*) generalized too sweepingly when they stated that "in the tannage with a dialdehyde, the dialdehyde penetrates the hide when the hide is in an acid condition and no tannage takes place."

In 2 *N* Na_2CO_3 solutions, i.e., at pH around 10, both malonaldehyde and succinaldehyde tan better than at pH 7, but only with the latter can the same T_s and the same leathering effect be reached as on the acid side. Malonaldehyde gives a horny yellow-brown product, shrinking at 68°C., before neutralization but at 75°C. afterwards. Succinaldehyde produced a leather than shrank at 78°C. before, and at 82°C. after neutralization. In both instances, lowering the pH below 7 raises the T_s, which demonstrates that optimum tanning conditions do not prevail on the alkaline side.

Glutaraldehyde.—This aldehyde, $OCH(CH_2)_3CHO$, unlike its two lower homologs, does not reach the peak of its tanning action on the acid side of the pH scale. For example, in one experiment, starting from pickled stock and ending at a pH of 4.5, we observed a maximum T_s of 80°C. By holding the pH of a depickled hide constant at pH 7 by means of $CaCO_3$, we succeeded in raising the T_s to 85°C. Subsequently lowering the pH to 4 caused the T_s to decline to 83°C. At pH 10 and above, glutaraldehyde is a better tanning agent than the two lower homologs, producing leather with a T_s of 84°C. In all these experiments 12 to 12.5% on the pickled weight of a 25% solution of glutaraldehyde was used.

Hydroxyadipaldehyde.—This aldehyde, $OCH(CH_2)_3CHOHCHO$, proved to be a very poor tanning agent. After tanning with it at pH 7.6 for three days, a T_s of only 69°C. was noted. In a second experiment, the T_s rose no higher than 73°C. after seven days. The leather curled up on drying and became horny and very stiff. In short, it had all the drawbacks noted for

leather tanned with glyoxal under similar conditions. In strong soda solutions the T_s rose 2° higher to 75°C., and the appearance of the tanned hide pieces also was improved.

Amounts of Aldehydes Fixed.—Methods used for the direct and indirect determination of this aldehyde have already been described. The first part of Table V presents figures which are typical for the formaldehyde

TABLE V

FIXATION OF ALDEHYDES BY COWHIDE

Exp't. No.	Type Cowhide	Per Cent of 100% Aldehyde Given*	Max. Ts,°C.	PER CENT ON DRY BASIS			FIXED ALDEHYDE†		
				Hide Subst.	Oil +Ash	Balance	Per Cent of Hide Subst.	Millimoles per g. Subst.	Per Cent of Aldehyde Applied‡
				FORMALDEHYDE (*Mol. Wt.* 30.03)					
1.	bend	3.6	92	92.4	5.9	1.7	2.2	.73	11
2.	side	1.8	91	98.9	3.3	(−2.2)	1.4	.46	15
3.	garment grain	3.6	89	96.7	2.7	0.6	2.0	.68	11
4.	side	1.8	90	97.6	2.2	0.2	1.6	.55	18
5.	garment grain	1.8	91	98.4	1.8	(−0.2)	1.9	.63	21
				GLYOXAL (*Mol. Wt.* 58.04)					
6.	bend	1.5	82	92.0	4.6	3.4	3.7	.64	49
7.	side	3.6	86	94.7	2.3	3.0	3.2	.52	17
				MALONALDEHYDE (*Mol. Wt.* 72.1)					
8.	bend	5.0**	77	96.2	1.3	2.5	2.5	.35	13
9.	garment grain	8.8††	79	93.3	2.7	4.0	4.4	.61	10
				SUCCINALDEHYDE (*Mol. Wt.* 86.1)					
10.	garment grain	2.7‡‡	82	95.1	1.4	3.5	3.7	.43	28
11.	garment grain	1.6‡‡	79	95.5	2.4	2.1	2.2	.19	27
				GLUTARALDEHYDE (*Mol. Wt.* 100.1)					
12.	garment grain	3.1	84	91.41	2.28	6.31	6.9	.69	45

*On drained pickled weight.
†For formaldehyde, determined directly; for all others, computed from "balance" on dry basis.
‡Assuming 20 per cent of the drained pickled weight to be hide substance.
**Calculated from ethoxypropane.
††Calculated from methoxypropane.
‡‡Calculated from diethoxytetrahydrofurane.

content of well rinsed leathers produced by us in alkaline solutions. Maximum fixation from direct determination of HCHO reached 2.2% HCHO on hide substance using 3.6% HCHO on drained pickled weight. As Table V shows, the sum of hide substance, oil, and ash leaves only a small balance

or may even exceed 100%. The reported upper limits of bound formaldehyde are of particular interest in view of the relatively low percentages of formaldehyde employed. The ratio of collagen to HCHO varied from 10:1 to 5:1. From the point of view of tannery economics this ratio is much more realistic than the ratios prevailing in previous experiments where similar pH ranges were explored (5b). Table VI shows a few figures for bound formaldehyde obtained in those earlier tests together with the ratio of collagen to formaldehyde and the "yield". The figures demonstrate that even by using inordinately high formaldehyde concentrations, essentially the same figures for bound formaldehyde were obtained, unless the amount of formaldehyde used exceeded that of collagen.

TABLE VI

MAXIMUM FIXATION OF FORMALDEHYDE BY COLLAGEN

(*Tanned 24 hours in 0.1 molar phosphate solutions*)

Highberger & Retzsch Reference (5b)	Ratio of Collagen to Formaldehyde	Final pH	FIXED FORMALDEHYDE		
			Collagen, %	Millimoles per g. Collagen	Aldehyde Applied, %
Table II, p. 135	2:1	10.02	2.31	0.77	4.6
Table V, p. 140	2:1	9.66	2.03	0.68	4.1
Table II, p. 135	2:3	9.86	3.03	1.01	2.0
Table IV, p. 139	4:1	9.82	1.84	0.61	7.4

We also used the ratio of 2 collagen : 3 formaldehyde in our tanning process, adding the formaldehyde to a 2 *N* Na_2CO_3 solution. In this experiment the fixation reached 4.8% or 1.6 millimols per g. collagen of which 18%, i.e., about twice the usual amount, was volatile on drying at 100°C.

DISCUSSION

Formaldehyde and Glyoxal.—Many workers in the tanning field have discussed the hazards of obtaining hard and cracky leather with a formaldehyde tannage (8,9,10). In practice the process most frequently resorted to consists of tanning at a comparatively low pH, where large excesses of formaldehyde must be applied in conformity with the mass action law, in order to achieve a tanning action. In fact, Theis and McLaughlin (11*a*) voice the belief that the increased fixation of formaldehyde at high pH values, adds "but little or nothing to the structural network of the collagen-formaldehyde compound . . . Practice has shown that leather produced in the pH range 5–8.5 is definitely superior to that produced at higher pH values regardless of the fact that more formaldehyde is fixed at the higher pH values."

The principal difficulty arises from the fact that dilute alkaline solutions cause the hide to swell just as dilute acids do. It is understandable that most of the theoretical work was unconcerned with this swelling action. As a direct consequence, however, the enormous number of theoretical investigations of the formaldehyde tannage at pH values up to 13 did not advance its practical use. Therefore, the observation of Küntzel (12) that Na_2SO_4 suppresses swelling in alkaline solutions, seemed worth exploring. We found only one basic study on formaldehyde, by Gustavson (13), that had employed Na_2SO_4/NaOH and Na_2SO_4/Na_2CO_3 systems. After some preliminary experiments it became clear to us why such systems are not satisfactory from the practical standpoint: the leather obtained is flat and tinny.

A startling improvement in the character of the leather was noted when we turned to the use of 2 *N* Na_2CO_3 in the tanning solutions. Before tanning, the hides or skins feel almost like pickled stock; the leather obtained has a strong grain, and is full and pliable, even without fatliquoring. Glyoxal leather differs from that made with formaldehyde only by its light tan color and by shrinking a few degrees lower.

Previous tanning experiments with glyoxal were not extended to the alkaline range because the Cannizzaro reaction was thought to preclude its use as a tanning agent in that region. The fact is, however, that even at pH 9.5 more than four hours must pass before glyoxal loses half of its strength (14). In the past only Winheim and Doherty (4*b*) and Kremen *et al* (15) were concerned with practical uses for glyoxal. The former received a patent based on the concept that only one of the aldehyde groups in glyoxal and other dialdehydes combines with the amino groups of the collagen, while the other is "free" and can react with suitable resin-forming monomers. Kremen *et al.*, on the other hand, were interested in the action of aldehydes on vegetable-tanned sole leather. They noticed a marked improvement of such stock by retanning with glyoxal, although it left much to be desired when used alone.

One step which is very important for the success of these tannages is the neutralization of the tanned hides in a fresh bath by the gradual addition of acid prior to washing or rinsing. Obviously, a washing process at a pH of 9 or higher has the same harmful effect as has tanning in more dilute alkaline liquors at this pH. Time and again substantial losses in strength have been observed after washing, indicating a weakening of the fiber structure because of the tendency for the outer layers, especially of the grain, to swell and to break away from the corium.

Tannage in the alkaline range, it seems, can proceed under three distinct states of swelling: in a flaccid state, as in the so-called alkaline pickle; in what we would call a natural state, which, we found exists in solutions of non-caustic alkalies of at least 1.5 normality; and in a state of tension and excessive swelling of the grain, which, of course, has been the condition from which the aldehyde tannages suffered in the past.

The possibility of by-passing the acid pickle by bringing bated stock directly in contact with strong soda solutions was not overlooked, since it would offer some advantages. A preliminary test indicated, however, that both formaldehyde and glyoxal would produce somewhat weaker leather when pickling was omitted.

Higher Aliphatic Dialdehydes.—Curiously enough, the first study on long-chain dialdehydes, by Gustavson (16), concerned itself with glycol derivatives with built-in oxygen bridges. Their affinity to collagen as measured by the T_s diminishes as the chain length increases. This order is reversed for malonaldehyde and succinaldehyde. Moreover, both tan better in a slightly acidic medium than at pH 7 or above. Malonaldehyde leather is canary yellow, while succinaldehyde produces a pleasing tan color. These colors are as unstable in sunlight, or under a fadeometer, as those of vegetable leather. Succinaldehyde leather is distinguished by a particularly smooth grain. In roundness and fullness it appears superior to any other aldehyde leather, including that produced by formaldehyde and glyoxal.

Glutaraldehyde probably marks a return to the more "normal" findings that aldehyde tannages are favored by an alkaline pH. Above pH 7 it raises the T_s higher than succinaldehyde, but on the acid side the picture is reversed. Still, glutaraldehyde produces fairly good leather of a light tan color even at pH 4–5.

Hydroxyadipaldehyde has too weak a tanning action to produce acceptable leather. A single hydroxy group next to the aldehyde group creates a powerful steric hindrance and prevents a leathering effect comparable to that obtained with an unsubstituted aldehyde.

Future studies will probably tell us at what chain lengths the affinity of aliphatic dialdehydes for collagen will taper off. The longer chain dialdehydes would not be expected to have the tanning effects of those already investigated. Two of the latter, glyoxal and glutaraldehyde, seem likely to be introduced into tannery practice. Although they are higher in cost than formaldehyde, they offer compensatory advantages: they do not irritate the mucous membranes, and they do not result in a white tannage which often is undesirable.

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DISCUSSION

Dr. Harold G. Turley (Rohm & Haas Co.): Dr. Seligsberger has offered some new contributions to this important field of aldehyde tannage. About 60 years ago, Pullman first patented the use of formaldehyde for tanning white leather. This enabled the tanner to produce new types of leather of greater commercial utility than had been produced previously with the oil tannage. White leather was used a lot in Europe, in military, naval, and police equipment, for belts and holsters, trappings and facings, and so on.

Dr. Seligsberger expressed some surprise that the high shrink temperature that can be obtained with formaldehyde, which indicates that it is an excellent tannage, should not have brought about a greater use of this tannage. I think we should caution you about a viewpoint that is quite common today, namely that the quality of the tannage is much controlled by the shrink temperature. Here is a very good example of a case where that is not so: formaldehyde tannage does make a heat-resistant leather, but it lacks an important attribute, the filling of the skin. In Dr. Seligsberger's tables you noticed from the indirect calculation of the amounts of aldehyde combined with the skin that there was a degree of tannage of from 2 to 5. Of course, a degree of tannage of 60% or more for vegetable leather is easily realized, and even with chrome tanning a degree of tannage of 20 is possible.

For a number of years there were not many contributions to the aldehyde tannage, except to find out that a number of aldehydes did not work, particularly the simple ones. About ten years ago there was some interest in the new dialdehyde, glyoxal. However, there was some disagreement as to its value, and Dr. Seligsberger has pointed out the conditions necessary to achieve a satisfactory glyoxal tannage. I think it is quite important from a theoretical point of view that Dr. Seligsberger has discovered that some of the lower aliphatic dialdehydes, namely malonic, succinic, and glutaric, are capable of

tanning leather in a fashion similar to formaldehyde. An interesting and novel approach is his idea of controlling the tanning action by tanning in strong solutions of alkali, in which, I suppose, there is an internal osmotic condition set up that is somewhat different from that produced on adding neutral salts, which has been customary, thus avoiding some of the common troubles of cracky grain and hard leather.

I hope this research on aldehyde tannages will continue, because it surely must be important to investigate the aldehydes of the dicarboxylic group, the unsaturated aldehydes, and the aromatic aldehydes. No matter what the outcome, whether valuable commercially or not, the work must inevitably contribute to our knowledge of the mechanism of tannage.

Dr. Seligsberger, have you formulated any ideas of a theoretical nature as to why the formaldehyde and glyoxal tannages are more favorable in the alkaline condition, while better results are obtained with malonic and succinic dialdehydes in a somewhat mildly acid condition? Then, to add a little to the problem, the glutaric aldehyde apparently tans well over a wide pH range.

DR. SELIGSBERGER: Dr. Turley, we have not developed any theoretical speculations about these points as yet.

DR. EDWARD M. FILACHIONE (Eastern Utilization Research Branch, U. S. Dept. of Agriculture): This paper was very interesting to us. We also have been doing some work on aldehyde tanning. We have been restricting our studies to the more conventional type of systems in alkaline solutions, and it is interesting to learn about the results presented in this paper. Is 2-normal sodium carbonate the optimum concentration?

DR. SELIGSBERGER: We did not find any great difference between 1.5-normal and 2-normal solutions. But we found that under certain practical conditions, for instance in the case of glyoxal, 2-normal would be the upper limit, because the Cannizzaro reaction is more pronounced in such a solution than in a solution of sodium carbonate and bicarbonate at a normality of about 1.5. The lower limit is about 1.25-normal. Below this, you approach the conditions prevailing in dilute solutions.

DR. FILACHIONE: You listed results obtained with 0.5-normal and 2-normal sodium carbonate. I wondered whether you had studied any intermediate concentrations.

DR. SELIGSBERGER: We have some in between.

DR. FILACHIONE: Is the effect of concentration as noticeable in the case of sodium bicarbonate?

DR. SELIGSBERGER: With sodium bicarbonate there are limitations because of its low solubility. We have not studied it alone. We have worked preferably with sodium bicarbonate as a means of depickling, reaching a pH

of about 8 with this mild alkali, and then adding sodium carbonate to raise the pH to 9.8 or 10.0, depending on the nature of the pickled hide which sometimes is slightly buffered.

DR. FILACHIONE: We are also interested in this system because of other treatments which are carried out most effectively in alkaline solutions.

DR. SEYMOUR S. KREMEN (Leather Research Corp.): With your new set of conditions, did you perhaps go back and review the corresponding mono-aldehydes of the same molecular weights, to see if they had improved tanning power?

DR. SELIGSBERGER: We have reviewed only one—propionic aldehyde—because we feel that some of the mono-aldehydes are such irritants that they will not assume any practical value. The propionaldehyde obviously tans a little better on the alkaline side. But it is not stable in alkaline solution. We have not studied the extent of the reaction taking place. We think that the other monoaldehydes also are rather short-lived under alkaline conditions.

DR. TURLEY: I cannot resist saying, apropos of this discussion of tanning in 10% sodium carbonate solutions, that it is mentioned in Procter's book that they made leather years ago by drumming skins in potassium carbonate solution. When dried out, the skins appeared to be leather. We are happy that, in this case, Dr. Seligsberger took the precaution of washing out the alkali, and finding that what he had left really was leather.

LEATHER CHEMISTS' ANNUAL CONFERENCE

The annual general meeting and conference of the Society of Leather Trades Chemists was held on September 21 and 22, at the University, Leeds. The conference was opened on Friday morning by Dr. R. G. Mitton, President, who extended a welcome to all present and particularly Dr. H. C. Holland from New Zealand. The first part of the afternoon was devoted to the Seventh Procter Memorial Lecture which was delivered by Dr. G. W. Kenner. Following this, came the annual general meeting of the Society, and among the important items considered was the adoption of the revised Official Methods of Analysis. These will be available in book form in the near future.

The Officers of the Society for 1956-7 are: President, Dr. L. Goldman; Vice-President, Dr. R. G. Mitton; Members of Council, E. F. Wallington, Dr. M. Horwood, W. Hannock, H. Lee, J. S. Mudd, Dr. T. White; Hon. Treasurer, Prof. D. Burton; Hon. Secretary, G. W. Humphreys. —*Leather World*, Oct. 4, 1956.

Specimens of Egyptian leather, dating back more than three thousand years, are to be found in the British Museum, and they retain all the characteristics of good leather. Roman sandals of the first century are not as finished exhibitions of the tanner's art as the old Egyptian leather, and yet they show sound knowledge of leather making.

—*Lactic Acid in Leather Manufacture*, Alan A. Claflin and Harry P. Corson. Boston: The Avery Chemical Company, 1920.

TANNING STUDIES WITH ALDEHYDES

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ABSTRACT

Calfskin and cattle hide which had been processed through the conventional pretanning operations were treated with eight different aldehydes. All the aldehydes included in this study underwent interaction with collagen and showed a tanning action as judged by elevation of the shrinkage temperature of collagen and stabilization of its fibrous structure. The shrinkage temperature of the hide substance was increased by treatment at pH about 7.5 to 8.0 to approximately 75°C. for succinaldehyde, 84°C. for glutaraldehyde, 82°C. for 3-methylglutaraldehyde, 78°C. for 2, 4-dimethyl-2-methoxymethylglutaraldehyde, 76°C. for α-hydroxyadipaldehyde, 80°C. for dialdehyde starch, and 72-74°C. for polymethoxy aldehydes. Formaldehyde and glyoxal (in bicarbonate solution) increased the shrinkage temperature of collagen to approximately 89°C. and 83°C., respectively. In weakly acidic solution glutaraldehyde appeared to be almost as reactive as formaldehyde toward collagen. The tanning action of dialdehyde starch, because of its potential availability at low cost, is of unusual interest.

INTRODUCTION

The tanning action of certain aldehydes, particularly formaldehyde, has been known for some time, and studies have indicated that tanning action is generally limited to the simpler aliphatic aldehydes (1–4). Formaldehyde, the simplest aldehyde, is the most reactive of this class of organic compounds, and its tanning action has been studied extensively by many investigators. Acetaldehyde, the next higher homologue, has a considerably weaker tanning action, and the higher homologues are lacking in this property (1). Among the unsaturated aldehydes, the simplest member, acrolein, and its next higher homologue, crotonaldehyde, have a tanning action, but this is lost if ethyl or propyl groups are introduced in the 2 and 3 positions of acrolein (4). With regard to dialdehydes, glyoxal, the simplest, is a fair tanning agent, particularly in organic solvents (5–8). Pyruvic aldehyde (methyl glyoxal) also shows tanning power (1,8) and in some solvents is considered comparable to formaldehyde (1). The literature suggests that malonaldehyde and succinaldehyde have tanning power(7,9). Some higher molecular weight dialdehydes, whose structures are equivalent to dialdehydes corresponding to certain polyethylene glycols, also have been investigated (9). These dialdehydes were of the following structure:

$$CHO\text{-}CH_2\text{-}(O\text{-}CH_2\text{-}CH_2)_n\text{-}O\text{-}CH_2\text{-}CHO$$

and have been conveniently termed monoglycol-, diglycol-, and triglycoldialdehyde where $n = 1$, 2, and 3 respectively. The simplest of these

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(monoglycoldialdehyde) was found to be a good tanning agent, increasing the shrinkage temperature (T_s) of collagen by 12°C. The tanning power decreased with increasing value of n, and was essentially absent in the dialdehyde corresponding to the structure where $n = 3$.

This paper reports the preliminary examination of several dialdehydes, namely succinaldehyde, glutaraldehyde, 3-methylglutaraldehyde, 2,4-dimethyl - 2 - methoxymethylglutaraldehyde, α-hydroxyadipaldehyde, and dialdehyde starch. Also examined were some monoaldehydes which may be termed "polymethoxy" aldehydes corresponding to the general structure CH_3- $(CH\text{-}CH_2)_n$ - CHO. For purposes of comparison glyoxal and formalde-

OCH_3

hyde also have been included.

EXPERIMENTAL

Materials.—Succinaldehyde, glutaraldehyde, 3 - methylglutaraldehyde, and α-hydroxyadipaldehyde were available as 25 to 50% aqueous solutions and were diluted to a concentration of approximately 5% prior to use. 2,4-dimethyl - 2 - methoxymethylglutaraldehyde polymerizes on standing, and the sample received was the polymer. However, this polymer readily reverted to the monomer on simple Claisen distillation in vacuum as recommended by the manufacturer (10). The monomer, freshly distilled at a pressure of about 5 mm., was dissolved in water to give a stock solution of about 15% aldehyde concentration. This was diluted to 7.5% when used in hide treatments.

Dialdehyde starch, also termed oxystarch, was a sample prepared by the electrolytic periodate oxidation of corn starch (11). Approximately 96% of the anhydroglucose units of the starch molecule were converted into the dialdehyde structure. Dialdehyde starch was solubilized by autoclaving a 10% suspension of this starch derivative in water at 120°C. for one-half hour.

The polymethoxy aldehydes were prepared from commercially available polymethoxy acetals (12) of the general structure CH_3 $(CH\text{-}CH_2)_n$ CH

OCH_3

$(OCH_3)_2$. Three grades of polymethoxy acetals, designated as PMAC - 5, PMAC - 10, and PMAC - 15*, were available; these differ in average molecular weight, which increases in the order listed. The acetals were hydrolyzed by mixing 10 g. of the acetal with 60 ml. of a 1% hydrochloric acid solution. The two-phase system was allowed to stand for 2 days or longer with occasional shaking. The PMAC - 5 dissolved almost completely upon hydrolysis, whereas in the case of PMAC - 10 and PMAC - 15 solution was not complete. The hydrolysis mixtures were then neutralized to a pH of 6–7 with about 3 g.

*The mention of specific brands or companies is not to be construed as an endorsement by the U. S. Department of Agriculture of these brands or companies over those not mentioned.

of sodium bicarbonate, and sufficient ethyl alcohol was added to the partially solubilized mixtures to effect complete solution of the organic phase. In preparing solutions greater than 10% in concentration, 10 g. of the polymethoxy acetal was hydrolyzed with 30 ml. of the 1% hydrochloric acid solution.

The hide materials were limed cowhide and pickled calfskin obtained from local tanneries. These were converted into acetone-dehydrated stock as described in an earlier publication (13).

Treatment with Aldehydes.—The following procedure was typical: Small strips, approximately 1″ x 3″, were cut from the acetone-dehydrated stock, and several of these, amounting to 5 to 15 g., were used for each treatment. The acetone-dehydrated strips were wet back in water and then blotted on towels. The strips were then placed in 100 ml. of the aqueous aldehyde solution, which generally was about 5% concentration with respect to the aldehyde. In the case of the polymethoxy aldehydes, however, 10 – 15% solutions were used because of their considerably higher molecular weights. The treatments were carried out at room temperature at various pH and salt contents, and agitation was provided by continuously rolling the bottles in which the treatments were made on a low-speed jar mill. Periodically the pH of the solution was determined, and a shrinkage-temperature specimen ¼″ x2″ was cut with a die from each strip. The remainder of the strip was returned to the bottle, and the T_s specimen was washed in running tap water for 24 hours. The T was determined on the freely suspended specimen mounted in a holder accommodating four samples. After shrinkage, the samples were immersed in cold water for evidence of reversible shrinkage. After 4 days of treatment, the remainder of the strips in the bottle were washed 24 hours in running water, allowed to air-dry, and examined for appearance.

RESULTS AND DISCUSSION

The data collected are summarized in Tables I and II.

In our studies the shrinkage temperature in the early stages of the reaction was obtained to enable a qualitative judgment of the rate at which the maximum T_s was attained and thus provide additional data concerning the overall relative reactivity of these dialdehydes toward hide substance. All the aldehydes included in this study showed a tanning action as indicated by elevation of the T_s of the aldehyde-treated hide material and by the leather-like drying of the products. Among the dialdehydes, as judged by the maximum shrinkage temperature of the treated cowhide and the rate of its attainment under various conditions, glutaraldehyde appeared to be the most reactive, and α-hydroxyadipaldehyde the least reactive, toward hide substance. The tanning power of 3-methylglutaraldehyde seemed to be almost equal to that of glutaraldehyde. These two glutaraldehydes appeared to be more reactive than succinaldehyde and glyoxal as indicated by the shrinkage temper-

atures attained after one and three hours of treatment under comparable conditions.

On this same basis 2,4 - dimethyl - 2 - methoxymethylglutaraldehyde appeared to be less reactive than glyoxal, although the products obtained from the trisubstituted glutaraldehyde, particularly in the pH range of 7 to 8, showed good leather characteristics. In the treatments with this dialdehyde at high pH, a gummy insoluble phase, probably a polymer, separated; how-

TABLE I

TANNING OF COWHIDE WITH ALDEHYDES

Exp't. No.	TREATMENT*					SHRINKAGE TEMPERATURE, °C., AFTER				
	Aldehyde	Conc.,%	Buffer	Salt	pH**	1 hr.	3 hr.	6 hr.	1 day	3 days
1.	Succinaldehyde	5	None	None	3.2–3.3	68	72	72	77	76
2.	"		None	NaCl	3.5–4.0	72	78	79	80	80
3.	"		$NaHCO_3$	None	6.9–7.4	68	71	71	73	75
4.	"		MgO	NaCl	9.1–8.8	68	75	74	75	78
5.	Glutaraldehyde	5	Lactic	NaCl	2.5–3.1	73	79	81	83	84
6.	"		None	None	3.4–4.2	70	81	—	84	86
7.	"		None	NaCl	3.8–4.7	77	82	82	83	—
8.	"		$NaHCO_3$	None	8.8–7.8	75	82	84	84	84
9.	"		MgO	NaCl	9.8–9.4	78	83	84	86	86
10.	3-Methylglutaraldehyde	5	Lactic	NaCl	2.7–3.1	72	77	79	81	82
11.	"		None	None	3.7–4.0	76	81	81	81	80
12.	"		None	NaCl	4.0–4.6	77	80	81	82	81
13.	"		$NaHCO_3$	None	8.0–7.7	75	81	82	82	81
14.	"		MgO	NaCl	9.4–9.0	77	80	80	81	81
15.†	2,4-Dimethyl-2-Methoxy-methylglutaraldehyde	7.5	None	None	4.6–4.4	65	65	66	70	69
16.†	"		$NaHCO_3$	None	8.2–7.7	65	69	71	75	78
17.†	"		MgO	NaCl	9.9–9.4	62	64	65	68	73
18.	α-Hydroxyadipaldehyde	5	None	None	4.5–5.1	62	65	—	69	72
19.	"		$NaHCO_3$	None	8.5–7.8	65	66	—	72	76
20.	"		MgO	NaCl	9.3–8.9	—	64	—	69	70
21.	Glyoxal	3	None	None	3.0–3.3	63	63	62	69	70
22.	"		None	NaCl	3.9–4.4	65	67	68	75	78
23.	"		$NaHCO_3$	None	8.1–7.3	71	77	78	76	81
24.	Formaldehyde	3	None	None	5.2–4.7	73	80	82	87	89
25.	"		$NaHCO_3$	None	9.2–8.9	75	83	86	86	88
26.‡	PMAC - 5	10	$NaHCO_3$	None	7.1–7.6	—	—	—	74	77
27.‡	"		MgO	Na_2SO_4	11.1–10.9	—	—	—	73	74
28.‡	PMAC - 10	10	$NaHCO_3$	None	7.3–7.7	—	—	—	70	72
29.‡	PMAC - 15	10	$NaHCO_3$	None	7.3–7.7	—	—	—	70	73

*Two or three strips (1" x 3") of cowhide (*Ts* about 63°C.) were treated with 100 ml. of the aqueous aldehyde solution. Where indicated, the salt content was 5%, the $NaHCO_3$ was 0.25 *M*, the MgO was 0.5%, and lactic acid 0.02*M* on the solution basis.

**Range of pH from 1 hour to 3 days.

†*Ts* of raw hide in these experiments was 60°C.

‡The polymethoxy acetal was hydrolyzed to the corresponding aldehyde prior to the experiment. The aqueous solutions contained 10-25% alcohol.

TABLE II

TANNING OF CALFSKIN WITH ALDEHYDES

Exp't. No.	TREATMENT* Aldehyde	Conc., %	Buffer	Salt	pH**	SHRINKAGE TEMPERATURE, °C., AFTER 1 hr.	3 hr.	6 hr.	1 day	3 days
1.	Succinaldehyde	5	None	NaCl	3.3–3.4	73	77	77	78	78
2.	"		$NaHCO_3$	Na_2SO_4	7.4–7.9	71	72	72	74	77
3.	"		Na_2CO_3	Na_2SO_4	9.2–9.1	71	75	74	77	77
4.	Glutaraldehyde	5	None	NaCl	3.9–4.3	80	82	83	83	83
5.	"		$NaHCO_3$	None	7.6–8.0	80	80	80	81	81
6.	"		$NaHCO_3$	Na_2SO_4	7.6–8.0	83	83	83	82	82
7.	"		Na_2CO_3	Na_2SO_4	9.6–9.5	70	75	78	83	83
8.	3-Methylglutaraldehyde	5	None	NaCl	4.1–4.3	78	80	80	80	80
9.	"		$NaHCO_3$	Na_2SO_4	8.3	82	82	82	82	82
10.	"		Na_2CO_3	Na_2SO_4	9.3–9.1	81	80	81	81	81
11.†	2,4-Dimethyl-2-Methoxy-Methylglutaraldehyde	7.5	None	NaCl	5.2–5.0	64	65	66	64	64
12.†	"		$NaHCO_3$	Na_2SO_4	7.9–8.3	69	75	76	74	72
13.†	"		Na_2CO_3	Na_2SO_4	10.3–9.6	74	79	79	78	76
14.†	Dialdehyde Starch	5	None	NaCl	5.1–5.3	68	72	73	76	79
15.†	" "		$NaHCO_3$	Na_2SO_4	8.1–7.8	72‡	—	75	79	81
16.†	" "		Na_2CO_3	Na_2SO_4	9.4–8.6	70‡	—	70	74	77
17.†	" "		MgO	Na_2SO_4	10.1–9.8	68‡	—	71	75	78
18.	Glyoxal	3	None	NaCl	3.3–3.5	59	61	62	73	77
19.	"		$NaHCO_3$	Na_2SO_4	7.6–7.4	73	77	79	80	83
20.	"		Na_2CO_3	Na_2SO_4	9.4–9.1	72	79	82	84	88
21.	Formaldehyde	3	None	NaCl	5.5–5.0	74	78	81	84	85
22.	"		$NaHCO_3$	Na_2SO_4	8.3–8.5	82	85	87	88	89
23.	"		Na_2CO_3	Na_2SO_4	10.2	82	84	85	87	89
24.††	PMAC-5	10	$NaHCO_3$	None	7.3–7.9	—	—	—	73	74
25.††	PMAC-10	15	$NaHCO_3$	None	7.6–8.0	—	—	—	68	72
26.††	PMAC-15	15	$NaHCO_3$	None	8.0–8.3	—	—	—	61	71

*Several strips (1″ x 3″) of calfskin (*Ts* about 65°C.) were treated with 50-100 ml. of the aqueous aldehyde solution. Where indicated, the salt content was 5%, and the $NaHCO_3$ and Na_2CO_3 were 0.25 *M* on a solution basis.

**Range of pH from 1 hour to 3 days.

†*Ts* of raw stock was 58°C. in these experiments.

††The polymethoxy acetal was hydrolyzed to the aldehyde. The aqueous solution contained 10-25% alcohol.

‡*Ts* after 2 hours of treatment.

ever this gradually dissolved during the course of the treatment. The air-dried specimens treated for the full length of time with the dimethylmethoxymethylglutaraldehyde yielded an almost white fibrous product.

In mildly acidic solution (pH about 4), the reactivity of glutaraldehyde toward cowhide approached that of formaldehyde. In contrast to the saturated aliphatic monofunctional aldehydes, which exhibit a rapid decrease in tanning power with increasing molecular weight, the tanning power of the saturated aliphatic dialdehydes appears to be maintained, at least in the series from glyoxal to the glutaraldehydes.

The tanned specimens obtained on treating cowhide or calfskin with succinaldehyde, glutaraldehyde, and 3-methylglutaraldehyde showed to a cer-

tain extent the property of reversible shrinkage, i.e., the heat-shrunken T_s specimen recovered a major portion of its shrinkage upon immersion in cold water. The reversibility of shrinkage was not as complete as that shown by formaldehyde-tanned specimens. In this property the behavior appeared to be similar to that of the glycoldialdehydes reported by Gustavson (9).

Treatment of cowhide in the presence of sodium bicarbonate with the dialdehydes investigated in our studies resulted in elevation of the shrinkage temperature to 84°C. for glutaraldehyde, 82°C. for 3-methyl glutaraldehyde, 81°C. for glyoxal, 75°C. for succinaldehyde, 76°C. for α-hydroxyadipaldehyde, and 78°C. for 2,4 - dimethyl - 2 - methoxymethylglutaraldehyde. Treatment of calfskin with these aldehydes gave similar results except that maximum Ts was generally reached in a shorter time than in the case of cowhide. Seligsberger and Sadlier (14), in a paper also appearing in this number of the Journal, reported that smooth-grained, soft, and pliable leather was obtained by tanning with formaldehyde or glyoxal in the presence of $2N$ sodium carbonate solutions. These authors found that malonaldehyde and succinaldehyde tanned best on the acid side, and that glutaraldehyde was effective over a wide pH range.

The data in Table II also show the tanning action of dialdehyde starch (oxystarch). Dialdehyde starch may be considered to be a polyfunctional aldehyde derived from the oxidation of the anhydroglucose units of the starch molecule to a dialdehyde structure. This material was of much interest in view of the recent development of an efficient electrolytic periodate oxidation process (11), which promises to make available a large variety of polyfunctional aldehyde derivatives from starch at potentially low cost. This process may be readily controlled to produce any given extent of oxidation of anhydroglucose units in the starch chain to dialdehyde structure. It was found that dialdehyde starch, 96% oxidized and solubilized by autoclaving at 120°C., readily interacted with calfskin, effecting a tanning action. The reaction appeared to proceed most rapidly in the pH region of about 8. Under these conditions, the shrinkage temperature of the calfskin was increased to about 80°C., and the reactivity of the dialdehyde starch appeared to be comparable to that of glyoxal.

The polymethoxy acetals, which have recently become available, are mixed methoxy acetals produced from methyl vinyl ether and methanol. The aldehydes derived from the acetals did show some tanning power, which was surprising since previous investigators have shown that the tanning action of the monofunctional aliphatic aldehydes decreases very rapidly with increasing molecular weight. Tanning action with these polymethoxy aldehydes was tested only in the neutral or alkaline pH range. The aldehydes from PMAC-5 appeared to be more active than those from the higher molecular weight polymethoxy acetals, increasing the T_s of cowhide by 14°C. The tanned specimens were quite stiff. By occasional working of the sample during the

latter stages of air-drying, however, a reasonably flexible leather-like material resulted, particularly from the treatment of calfskin with the aldehydes corresponding to PMAC-5.

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The authors wish to express their gratitude to Carbide and Carbon Chemicals Corporation for the samples of succinaldehyde, glutaraldehyde, 3-methylglutaraldehyde and α-hydroxyadipaldehyde; to General Aniline and Film Corporation for the samples of the polymethoxy acetals, PMAC-5, PMAC-10, and PMAC-15; to Shell Development Company for the sample of 2,4 - dimethyl - 2 - methoxymethylglutaraldehyde; and to the Northern Utilization Research Branch, U. S. Department of Agriculture, for samples of dialdehyde starch.

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Received October 8, 1956.

Leather, indeed, is often mentioned as one of the earliest materials for writing upon, though there is considerable doubt whether such leather was in any sense "tanned", and in many cases there is no doubt at all that the material referred to was very closely similar to our present parchment.

—*The Manufacture of Leather*, Hugh Garner Bennett. New York: D. Van Nostrand Company, 1910

CALCULATION OF STRETCH FROM BALL BURSTING STRENGTH DATA

I. D. Clarke and E. H. Harris

*Eastern Regional Research Laboratory**
Philadelphia 18, Pennsylvania

ABSTRACT

Methods are given for calculating elongation of the diameter of a circular test specimen, and increase in area of the specimen, from data obtained in the ball burst test. A table is given for obtaining elongation from plunger rise when the orifice diameter is 0.75" and the plunger diameter is 0.25".

INTRODUCTION

The official American Leather Chemists Association method for measuring stretch or elongation is Method E17. This method specifies the use of a tensile strength specimen (unless the sample is too narrow) and measurement of stretch by means of a tensile strength testing machine either at failure of the specimen or at some lower load.

The ball bursting strength testing machine, developed by the Quartermaster Leather Laboratory, was designed to measure stretch as well as strength, but the official method, E14, does not include the stretch measurement, nor is it included in Method E17. The illustration, Figure E14A, shows a thickness gage mounted on the lower anchor. This gage measures the movement or rise of the plunger during a test, and this rise is related to stretch of the specimen. It is not, however, directly proportional to the stretch.

Distension of the specimen or stretch has frequently been observed when making burst measurements. Bradley (2) apparently was the first to apply this type of test to leather. He devised a tester in which the leather was clamped over an orifice and pressure was applied to the lower side of the leather by rise of a steel ball. For interpreting his results he used the expression $Z = a\,p^n$, where Z is the height of rise of the ball, p is the pressure on the specimen, and a and n are constants characteristic of the leather.

Merrill (3) used a modified Mullen tester with hydraulic pressure under the rubber diaphragm. In this test the distorted leather is more like a segment of a sphere rather than a truncated cone with a spherical tip as in the ball burst test. He measured the vertical height of displacement of the center of the leather specimen, a measurement corresponding to that of rise of the plunger in the ball burst machine, and calculated the increase in area of the distended leather.

*A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, United States Department of Agriculture.

Boor and Niedercorn (1), who used a type of tester quite similar to those of Bradley and the ALCA, calculated both percent elongation* and percent increase in area. Their calculations are equivalent to that described below, but are more complex. They state that since in the range of height of break shown by most commercial leathers (0.3″–0.7″) these functions are nearly linear, the reading of height will serve as an index of either elongation or increase in area for routine testing.

The relation is not linear in the region where grain cracking usually occurs, and since it is only approximately linear outside of this region, it is desirable to express the results as percent stretch if possible.

As an illustration of the difference that would result from the use of plunger rise instead of percent stretch, the following data are taken from a test referred to later in this paper. Measurements of ball burst stretch at grain crack were made on cowhide specimens, half of which had been treated in various ways and the remainder left untreated. The stretch values of treated specimens were then divided by the values for corresponding untreated specimens. These ratios ranged from 0.21 to 0.42, whereas if they had been based on plunger rise the range would have been from 0.44 to 0.63. Corresponding ranges for stretch at burst were 0.51 to 0.74 and 0.69 to 0.83.

CALCULATION OF STRETCH FROM PLUNGER RISE

Calculation of stretch from plunger rise must of course be based on the dimensions of the apparatus being used. The calculations below have been made for a tester having the dimensions specified in Method E14, i.e., an orifice diameter of 0.75″ and a plunger ball diameter of 0.25″. In Figure 1

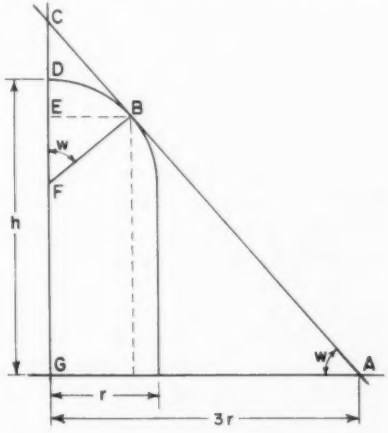

FIGURE 1—Diagram showing stretched length of a radius of the test area when plunger has risen the distance, *h*. Leather assumed to have 0.0 thickness.

*That is, the percent elongation of a diameter of the circular specimen.

the line AG represents one radius of the disk of leather under test before pressure has been applied to it, and the line ABD represents this same radius after the plunger has been raised the distance GD (denoted by h) so that the leather forms the angle GAB (w) with its original position. Using r to denote the radius of the ball (0.125″), the following equations for stretched length, d, and plunger rise, h, are readily derived:

$$d = AB + BD = (3r - BE)/\cos w + BD =$$
$$(3r - r \sin w)/\cos w + \pi r w/180$$
$$h = GC\text{-}DC = 3r \tan w - (FC\text{-}r) = 3r \tan w + r - r/\cos w$$
$$\text{Stretch, } \% = 100\ (d-3r)/3r = 266.7\ (d-0.375)$$

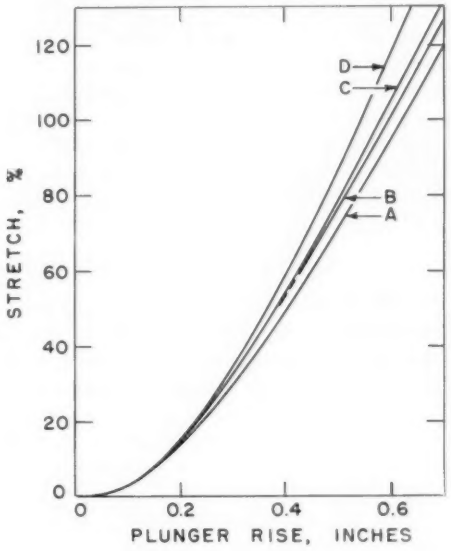

FIGURE 2.—Curves showing percent elongation or area increase as a function of plunger rise. Curves A, B, C, elongation calculated for leathers having thicknesses of 0.0, 0.10, or 0.15″ respectively. Curve D, percentage area increase for leather of 0.0 thickness.

Values of d and h for various angles were calculated, after which curve A, Figure 2, was drawn. Percentage stretch for various values of h can be read from the curve, but a table is easier to use if the number of items is small; therefore, Table I was prepared.

The above calculations assume ideal conditions. They ignore nonhomogeneity of the leather over the test area, thickness of the specimen, indentation of the plunger in the flesh side of the specimen which affects the height measurement, curvature of the specimen at A (Figure 3), which results in a small error in the effective orifice diameter measurement, and other effects of less importance. The thickness of the specimen is of the same order of magnitude as the radius of the plunger ball; additional calculations, there-

TABLE I

BALL BURST STRETCH*

Plunger Rise, *h*, inches	Stretch, %	*h*, inches	Stretch, %	*h*, inches	Stretch, %	*h*, inches	Stretch, %
0.03	0	0.20	14	0.36	41	0.52	76
.04	1	.21	15	.37	43	.53	79
.06	1	.22	17	.38	45	.54	81
.07	2	.23	18	.39	47	.55	83
.08	2	.24	20	.40	50	.56	85
.09	3	.25	21	.41	52	.57	88
.10	4	.26	23	.42	54	.58	90
.11	4	.27	25	.43	56	.59	93
.12	5	.28	26	.44	58	.60	95
.13	6	.29	28	.45	60	.61	97
.14	7	.30	30	.46	62	.62	100
.15	8	.31	32	.47	65	.63	102
.16	9	.32	34	.48	67	.64	104
.17	10	.33	36	.49	69	.65	107
.18	12	.34	37	.50	71	.66	109
.19	13	.35	39	.51	74	.67	112

*These values hold only for tests made with a 0.75″-orifice and 0.25″-diameter plunger, as specified in ALCA Method E14 (1953).

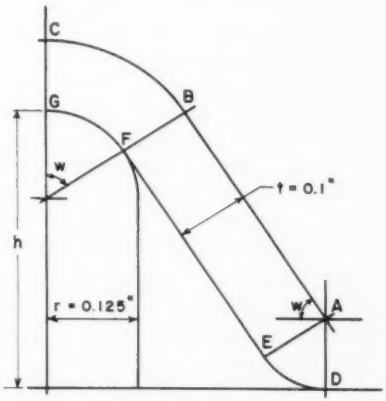

FIGURE 3.—Diagram showing stretched length of a radius of the test area when plunger has risen the distance, *h*. The leather is assumed to have a thickness of 0.1″.

fore, were made in which leather thickness (t) was included. Figure 3 is similar to Figure 1 except that in this case the leather is assumed to have a thickness of 0.1″. Making the assumptions that *BC*, *DE*, and *FG* (Figure 3) are

arcs of circles and that the bend of the leather at *A* is sharp, the following equations were derived:

$$d = [3r - (r + t) \sin w]/\cos w + \pi (r + t)\, w/180$$
$$h = 3r \tan w + r + t - (r + t)/\cos w$$

The stretched length, *d*, applies to both the grain and flesh sides of the leather because the distance *ABC*, Figure 3, is equal to the distance *DEFG*. This calculation does not take into account compression of the leather by the clamp with shortening of the distance *AD*. From the appearance of the specimens this is quite a localized effect and perhaps has little effect on the stretch behavior. Calculations with the above equations, assuming thicknesses of 0.10″ and 0.15″ were made, and these data are plotted as curves *B* and *C* in Figure 2.

Calculations also were made of increase in area of the test portion of the leather, basing the calculations on the relations shown in Figure 1. Curve *D*, Figure 2, presents these results. This curve has the same general shape as the stretch curves.

For leather 0.15″ thick (9½-ounce) the inclusion of thickness in the equations would increase the stretch values by 10 or 12%. For example, a value of 56% would be found instead of 50, or 28 instead of 25, as would be found if thickness were ignored. For thinner leathers the differences would be decreased proportionally. Thickness, however, decreases during a test by an unknown amount so that an exact calculation cannot be made.

During a test the dial showing plunger rise can be read only to about 0.01″ because of such factors as operator reaction time and the fact that usually the plunger does not break through instantly but pushes through gradually. A rise of 0.01″ corresponds to a stretch value of approximately 1% in the low stretch range and 2% or more in the high range. Thus it appears that the error resulting from failure to correct for thickness is often little, if any, greater than experimental error. The best procedure therefore appears to be to use the values for stretch given in Table I, recognizing that they may be a trifle low for thick leathers.

RELATION BETWEEN BALL BURST STRETCH AND ELONGATION

Ball burst stretch and elongation are both measures of the ability of leather specimens to increase in length or area under stress. Elongation values, however, should be greater than ball burst stretch values because they are measured on a narrow specimen with cut edges on each side of the test area, whereas the ball burst specimen has no cut edges in this area.*

Some comparative data by the two tests have been obtained in the course of other work and are given below. Results are given for acetone-dehydrated

*When the narrow tensile strength specimen is stretched, its width decreases as its length increases, because the cut edges on each side are not restrained by clamps. This results in greater elongation at grain crack than is obtained in the ball burst test where the specimen is clamped all round and is stretched in all directions, not just in one.

cowhide (untreated hide) and for this hide material after treatment with certain epoxides, aldehydes, or other tanning agents (treated hide). An effort was made to have as small a test area as possible for a given comparison, but the distance between these test locations varied from 1.5″ to 3″. Elongation was measured on a small specimen with a test area 1 cm. instead of 0.5″ wide and 2.5 cm. instead of 2.5″ long. The results are given in Table II.

TABLE II

COMPARISON OF BALL BURST STRETCH AND ELONGATION VALUES FOR UNTREATED AND TREATED COWHIDE

Test No.	UNTREATED HIDE (1) Ball Burst test	UNTREATED HIDE (2) Elongation test	UNTREATED HIDE Ratio 1:2	TREATED HIDE (1) Ball Burst test	TREATED HIDE (2) Elongation test	TREATED HIDE Ratio 1:2
I Average stretch at rupture,* $\bar{x}$, %	30.9	63.0	0.49	38.5	50.4	0.76
Standard deviation, s	10.2	7.5		10.0	9.4	
Coefficient of variation, $\bar{x}/s$, %	33.0	12.0		26.0	18.7	
II Average stretch at rupture,† $\bar{x}$, %	42.9	60.1	0.71	28.5	42.6	0.67
Standard deviation, s	4.8	6.8		5.1	8.3	
Coefficient of variation, $\bar{x}/s$, %	11.3	11.3		17.9	19.5	
II Average stretch at grain crack, %	31.0	58.3	0.53	12.5	30.6	0.41

*Average of duplicate measurements on 50 specimens (10 treatments).
†Average of duplicate measurements on 44 specimens (11 treatments).

In test I, ball burst stretch results were more variable (higher coefficient of variation) than those for elongation, but in test II there was little difference. For the untreated hide the ratio of stretch to elongation was not constant for the two tests; the ratios were 0.49 and 0.71. Correlation between results by the two tests was low; the coefficient, r, was 0.25 in test I and only 0.08 in test II. This low correlation was not related to direction of measurement of elongation as there was little difference in either standard deviation or correlation coefficient when these were calculated using elongation parallel or perpendicular to the backbone.

For the treated specimens the ratio of ball burst stretch to elongation was 0.76 in test I and 0.67 in test II. The range in ratios for the entire 21 treatments was from 0.61 to 0.79, and the values of r were 0.75 in test I and 0.72 in test II. It therefore appears that for this type of treated material ball burst stretch is approximately 70% of elongation. Whether this value is of general

applicability or sufficiently constant for many purposes can only be determined by further, carefully controlled work.

The ratios of stretch to elongation at grain crack varied considerably. For 11 lots of acetone-dehydrated hide, they ranged from 0.44 to 0.63; and for 11 lots of treated hide specimens, from 0.30 to 0.72. These larger variations might be expected because cracks were difficult to observe on a majority of these specimens, which were white untanned skin or white leather. Also, cracks first appear over the tip of the plunger in the burst test, and this area is less than half of that over which they may be found in the tensile specimen.

SUMMARY

Distension of the specimen during a ball burst test measured by height of rise of plunger has been calculated as percent stretch. A few comparisons of such stretch values with elongation values measured on a tensile specimen are reported. Agreement for raw skin specimens was lacking but was fair for tanned specimens.

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Received October 18, 1956.

"THE LEATHER WORLD" TO BECOME HOUSE JOURNAL OF THE LEATHER INSTITUTE

"The Leather World" is to cease publication with the issue of Thursday, December 27, 1956, as a weekly trade paper.

Arrangements are being made whereby the title of "Leather World" will be transferred to the Leather Institute. The Institute intends to publish an entirely new magazine, bearing that title, to appear at monthly intervals and commencing in January, 1957.

The new "Leather World" will in no way be a continuance of the present trade paper, except in name. It will be the official journal of the Leather Institute and issued free of charge. Its function will be to further the interests of the Leather Industry and its allied industries in every appropriate way. Important among its functions will be the task of bringing home to manufacturers and retailers of leather products ways and means by which they can profit by tying up with leather publicity and the promotional schemes which the Institute launches from time to time. —*Leather World*, Sept. 27, 1956.

Unto Adam and also his wife did the Lord God make clothing of skins and clothe them. —*Gen.* 3:21.

LIFE LINES

Brief Biographies of Our Contributors

Dr. S. K. Bose, coauthor with the late Prof. B. M. Das of an article that appeared in the December, 1956, issue, was born in West Bengal, India. He graduated in science from the University of Calcutta, and then joined the Department of Biochemistry, Indian Institute of Science, Bangalore, where he remained for about six years. He earned his M.Sc. and Ph.D. degrees from the University of Bombay by submitting theses. Next he joined the Department of Biochemistry, Central Food Technological Research Institute, Mysore, and carried out researches in biochemistry for about four years. Since 1953 he has been head of the Biochemistry Department, Central Leather Research Institute, Madras. He has published many papers on the biochemistry of proteins, fats, and enzymes, with special reference to leather manufacture, and has developed several biological processes, covered by Indian patents, which are of value to the leather industry. He is an Associate of the Royal Institute of Chemistry, London, and a member of the Society of Biological Chemists, India.

Ira D. Clarke.—See the November, 1956, issue of *JALCA*.

Martin L. Fein received his B.S. and M.S. degrees from Temple University. Before transfer to the United States Department of Agriculture in 1941, he worked with the Synthetic Fuel Group at the U. S. Bureau of Mines in Pittsburgh. From 1941 to 1953, at the U. S. Department of Agriculture's Eastern Utilization Research Branch, he studied the preparation and evaluation of various derivatives of lactic acid. In 1953 he transferred to the Hides, Tanning Materials and Leather Section of the same Branch, where he is conducting research on the chemical modification of hide substance.

Dr. Edward M. Filachione.—See the November, 1956, issue of *JALCA*.

Edward H. Harris.—See the November, 1956, issue of *JALCA*.

Charles J. Sadlier, a graduate of Holy Cross with a major in chemistry, joined the Quartermaster Corps late in 1954. Prior to this, he did graduate work at Northeastern University and was associated with the Engineering Department of the Lowell Technological Institute Evening Division.

Dr. Ludwig Seligsberger, a native of Fuerth, Germany, received his Ph.D. at the University of Erlangen, Bavaria, and in 1928 joined the staff of Professor M. Bergmann, Director of the Kaiser Wilhelm Institute for Leather

Research in Dresden. Six years later, because of political conditions then prevailing, he accepted a position in the chemical laboratory of a valonia extract factory in Izmir, Turkey. In 1937 he entered the United States and became chief chemist of the New Castle Specialty Division of the Allied Kid Company, Wilmington, Delaware. While there, he published six papers in this Journal, all of which dealt with problems of chrome tanning. Since 1954 he has been associated with the Leather Technology Laboratory Branch of the Quartermaster Research and Development Command, Natick, Massachusetts.

PROCEEDINGS OF THE PERKIN CENTENNIAL

All the papers presented during the Perkin Centennial will be printed in one volume bearing the above title. A copy will be sent to every registrant; others may obtain copies for $10 each from Richard R. Frey, Assistant Secretary A.A.T.C.C., Lowell Technological Institute, Lowell, Massachusetts.

The methods of (medieval) Florentine tanners would seem to have been much as follows: The raw hides were first salted to check putrefaction, limed in weak lime liquor and brought to a suitable condition for dehairing and fleshing, within somewhere about three months. Then they were placed between layers of coarsely ground oak bark in pits until full, when a thick topping of bark was put over them. No water or any other kind of liquid was allowed to get into the pits. These packs were taken up and reversed several times, fresh oak bark being introduced. This kind of tanning occupied somewhere about 18 months . . . The next process was 'handling', in which the hides were transferred to larger pits, and then turned over every day in a liquid or ooze made of oak bark. This process lasted five or six weeks. In later times robbia and other dyes in liquid form were introduced into the tanning process, so as to thoroughly saturate the skins which it was wished to finish colored or dyed. For the last manipulation the skins were hung over big wooden bars immersed in the taning-dyeing medium.

—*Guilds of Florence*. Edgecombe Staley. London: Methuen & Co., 1908.

The Great Council at Aix (A.D. 809) seems to have turned aside from its consideration of weighty doctrinal disputes in order to prohibit monks from wearing any gloves but those made from sheepskin, deerskin gloves being reserved for bishops.

—*Gloves and the Glove Trade*, B. Eldred Ellis. London: Sir Isaac Pitman & Sons Ltd., 1921

* * *

The art of leather-dressing was certainly practised in many of the monasteries, and possibly glove-making may have also furnished occupations throughout the country, but the earliest references to gloving as a craft in England do not occur until much later (than the 10th century).

—Ibid.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

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The officers and Council of the Association join the editorial staff in extending to all members the warmest of season's greetings and sincere wishes for a happy, prosperous, and peaceful New Year.

REPORT OF THE TECHNICAL COMMITTEES

October 16, 1956

The following is a brief summary of the current activities of the technical committees of the Association:

VEGETABLE LEATHERS COMMITTEE

Arthur N. Kay, *Chairman*

Subcommittees which have been working on the determination of (1) moisture and (2) fat (solvent extract) have been consolidated into one committee under Mr. Blair. Since the reorganization, the subcommittee has nothing to report.

Tannin Analysis Subcommittee.—Edward L. Rayfield, *Chairman*

The subcommittees under Mr. Jany and Mr. Dahl are carrying on continued activities on determination of lignosulfonates. They are in the process of selecting a second promising method to investigate. Mr. Dahl is at present preparing a report covering last year's work.

Since the annual meeting in June, Mr. Wagoner's Method for the Preparation of Solid Tanning Extracts has been published, and a subcommittee has been conducting further experiments on this method.

PHYSICAL AND MECHANICAL PROPERTIES COMMITTEE

E. D. Compton, *Chairman*

Water Penetration Subcommittee.—R. M. Lollar, *Chairman*

A set of tests on end point detection using Bavon-treated leather is just completed. These tests are similar to those on which the subcommittee report published in the July Journal was based.

A second series of tests using a waterproofing material supplied by Mr. Hopton is being run.

Lightfastness Subcommittee.—E. D. Compton, *Chairman*

This committee has nothing to report since the June meeting.

PREPARATORY AND POSTTANNING PROCESSES COMMITTEE

W. T. Roddy, *Chairman*

Oils and Fats Subcommittee.—R. M. Koppenhoefer, *Chairman*

Samples are being exchanged between Nopco and Socony Mobil laboratories for the purpose of determining the reasons for the disagreement in previous results.

A new set of samples being prepared by the Tanners' Council Laboratories will be sent out to all members in the near future.

STANDARDS AND SPECIFICATIONS COMMITTEE

C. Telander, *Chairman*

The Standards and Specifications Committee is currently discussing a proposed change in specifications for PNP determination and a request for change in method of analyses for oil and moisture for sole leather. An evaluation of the data accumulated in regard to the question of sampling area vs. weight in sole leather is also awaiting completion. This latter is in the hands of Charles Mann.

There is no other pending matter at this time.

TANNERY PRACTICE COMMITTEE

J. F. Wagoner, *Chairman*

The Tannery Practice Committee has no work ready to be reported at this time.

MECHANICAL LEATHERS COMMITTEE

H. V. Krakowski, *Chairman*

The Mechanical Leathers Committee has undertaken two studies:

1. A study of the heat resistance of mechanical leathers. At the present time, several chosen tannages are being evaluated.
2. An attempt to develop a hardness measuring device. The members of the committee feel that the shore durometer which is commonly used in the rubber trade is not satisfactory for measuring hardness of leather.

EVALUATION OF RAW STOCK COMMITTEE

William Cox, *Chairman*

The committee is continuing its studies on (1) the cure quality and (2) leather-making substance.

LEATHER FINISHES COMMITTEE

Bernard Roll, *Chairman*

A method for measuring the bleeding characteristics of leather was published in the July Journal. Some criticisms of the method have been made. The committee is considering these criticisms.

M. MAESER

President-Elect, ALCA

COUNCIL MEETING MINUTES

OCTOBER 10, 1956

National Bureau of Standards
Washington, D. C.

Through the courtesy of the Bureau of Standards, the meeting was held in their conference room. The meeting was called to order at 9:30 A.M. by President Thorstensen. All Council members were present plus Messrs. Merrill, Wederbrand, and O'Flaherty.

Minutes of Past Meetings.—The minutes of the Council meetings of June 17 and 20 were approved as corrected and ordered published.

Ways and Means Committee.—Mr. Wederbrand reported in great detail on his visit to Lake Placid and presented plans for the utilization of space for exhibits at the annual meeting June 2 - 4, 1957. Upon motion by Mr. M. Maeser, seconded by Dr. R. Stubbings, the plan was approved by unanimous vote.

Upon motion by Mr. R. Weldon, seconded by Dr. R. Stubbings, it was moved that the full report made by Mr. Wederbrand be placed in the hands of the Convention Committee, who should use it for publicity and to inform members.

The matter of fees for the booths and a plan of room allocation to members and space to exhibitors as suggested by Mr. Wederbrand was approved by Council and the matter left in the hands of the committee.

Convention Committee.—Mr. Retzsch was unable to attend the Council meeting. Dr. Stubbings, cochairman, reported the personnel of the committee.

Clinton Retzsch, *Chairman*
Robert Stubbings, *Cochairman*
Joseph Casnocha
Harold Bernard
Joseph Stellmach
William Hammel
Marden Lindsay
Mrs. Harold Bernard

This was approved by Council. Mr. Retzsch is to prepare a budget and submit it at the next Council meeting.

Convention Program.—Consideration was given to having advertising space in the program much like in the directory. Upon motion made by Mr. Wederbrand, seconded by Mr. Maeser, and carried, the matter was tabled for the time being.

Technical Committees.—President-Elect M. Maeser, as Coordinator of the Technical Committees, reported on the programs of the several committees. He will put this in a brief report which will become a part of these minutes.

Physical Testing Committee.—Mr. Maeser indicated his desire to resign as chairman and recommended Dr. Ell Dee Compton to succeed him. This recommendation was seconded by Mr. R. Stubbings and unanimously carried.

Considerable discussion followed regarding the relationship of this committee and the Joint ALCA-ASTM Committee. Dr. Compton is to take this into consideration in reorganizing the ALCA Physical Testing Committee.

Hide Powder.—Mr. Maeser reported that a new lot of standard Hide Powder had been completed and was now being analyzed by the committee. This committee is to make its recommendation to Council who will then make the final decision and advise Mr. Marshall.

Lignosulfonate Method.—This is now a provisional method but some corrections were suggested by Mr. Jay. This is to be referred to the chairman of the subcommittee which wrote the method, so that changes can be made, if desired, before the method is considered for official status.

Finish Method K12.—The result of a letter ballot was reported to Council. This method has been approved for provisional status. A number of comments were made by members, and these have been passed along to the chairman of the Leather Finish Committee by Mr. Maeser.

Method J40.—Sampling of Tannery Chemicals has not been published but was included in the index. Mr. Maeser has agreed to provide copy of this method so it can be published and distributed to members.

Memorandum of Agreement on Editorship of Journal.—As noted in the minutes of Council meeting of June 17, 1956, Dr. Flinn was authorized to sign this agreement on behalf of the Association. He has not done so up to this time, and therefore Council by motion of Dr. R. Stubbings, seconded by Dr. E. D. Compton, and carried by unanimous vote, authorized President Thorstensen to represent the A.L.C.A. and to get the agreement properly signed.

Journal.—Editor-in-Chief Merrill reported on the status of the Journal as follows: Manuscripts on hand March 1 were seven; he received by October 3 twenty more. He published twenty-one in May through November, leaving a total on hand of six. Two have been accepted for the December issue and four are being revised. This does not include translated articles, annual meeting speeches, and committee reports, except such committee reports as comprise new work and are of the nature of a paper. The Perkin Centennial symposium presentations are considered to be one paper. There are five presumably acceptable papers presented at the Mackinac meeting that have not been received; also one paper from the 1955 meeting has not yet been received. Assuming that all the papers now being revised are ultimately accepted, and that all six of the papers from the 1955-1956 annual meetings come in, we have enough material to carry us through March by holding down to three papers per issue. More papers are needed urgently, to provide a backlog and to permit greater flexibility in making up each issue.

Dr. Merrill brought up for discussion the desirability of appointing an associate editor. After much discussion on motion by Mr. Maeser, seconded by Dr. Compton, it was moved that the plan was approved in principle and that Dr. Merrill should consult with his Editorial Board and bring in some specific recommendations for consideration at the next meeting. Carried by unanimous vote.

Spanish Article.—After consideration, it was suggested to the Editor-in-Chief that he consider the possibility of having the abstract portion of published articles translated into Spanish. The matter was left in the hands of the Editor-in-Chief.

New Members.—Mr. Alfred N. Compton, Jr., of E. F. Houghton & Company, was elected to active membership.

Mr. Charles T. Cares' membership was transferred from associate to active status.

Membership in IULCS.—Council approved the application of the Leather Technologist Association of India for membership in the International Union of Leather Chemists Societies.

Perkin Centennial.—Dr. Compton reported a very successful meeting and gave much credit to the panel members.

Methods Procedure.—It was noted in the September, 1956, issue of the Journal of the Society of Leather Trades Chemists that a committee has been formed to look toward streamlining the procedure for adopting methods. This was referred to President-Elect Maeser for consideration.

Directory.—It was reported by the Secretary that the 1956 Directory has been mailed to all members.

Award Committee.—President Thorstensen announced the following appointments, and they were approved by Council:

J. H. Highberger
H. B. Merrill
G. W. Schultz

Nominating Committee.—President Thorstensen announced the following appointments, and they were approved by Council:

Arthur N. Kay
Dominic Meo
Reuben Henrich

Next Meeting of Council.—It was agreed that Council will meet the day previous to the Wisconsin Tanners Production Club in January in Milwaukee.

The meeting was adjourned.

Respectfully submitted,

FRED O'FLAHERTY
Secretary

CONVENTION NOTICE

The 1957 meeting of the American Leather Chemists Association will be held at the Lake Placid Club, Lake Placid, New York, on June 2–5, 1957. Since the convention committee would like to arrange the program as soon as possible, it would appreciate receiving brief abstracts by February 28 of papers to be presented. The abstracts should be sent to:

CLINTON E. RETZSCH, *Chairman*
Convention Committee
c/o Nopco Chemical Company
Harrison, New Jersey

The early tanneries were strange primitive establishments. The vats were oblong boxes, sunk in the ground, close to the edge of the town brook at the point where it crossed the main street. They were without either covers or outlets. The beamhouse was an open shed, within which old, worn-out horses circulated around while the bark was crushed at the rate of half a cord or so a day by alternate wooden and stone wheels, moving in a circular trough 15 feet in diameter.

—*Three Episodes in Massachusetts History, II.* Charles Francis Adams. Boston, 1892.

Discussing tanning as an integral part of colonial life, Percy W. Bidwell in his "Rural Economy in New England at the Beginning of the Nineteenth Century", contained in Transactions of the Connecticut Academy of Arts and Science (April, 1916, Vol. XX), writes: "A tannery or two seems to have been uniformly a part of the economic outfit of the inland town. The working dress of the people was largely composed of leather garments, not only their shoes and leggings, but shirts, breeches and coats as well. A large part of the material came from the hides of animals slaughtered on the farm and prepared at the village tannery. This was a primitive affair, quite on a par with the mills (grist, cider, and fulling mills) in the size of its plant and in the scope of its operations."

—*Economics of Cattlehide Leather Tanning.* Merrill A. Watson, D.C.S. Chicago: Rumpf Publishing Co., 1950.

* * *

(In the Roman era) Costumes of soldiers and of many civilians were usually completed by a leather cap, and the type of leather shoes worn indicated the rank of the wearer. Roman Senators wore one type of shoe in the summer and another in the winter . . . In summer, sandals or light-weight shoes were worn, but with the full dress or toga, the Calceus had to be worn. This was essentially a shoe with slits at the sides and straps knotted in front. Patricians generally wore such shoes made of red leather, while Roman soldiers wore heavy hobnailed sandal boots made with a number of straps wound round the lower part of the leg.

—Ibid.

ABSTRACTS

Vanadometric Determination of Hydroquinone, Tannin, and Hydroxylamine. Z. P. Suranova. *Trudy Odessk. Univ. Shornik Khim. Fakul'teta*, **3**, 73–76 (1953); *Chem. Abstr.*, **50**, 12759*d*.

Specific Determination of L-Hydroxyproline in Biological Materials. A. E. Pasieka and J. F. Morgan. *Proc. Soc. Exptl. Biol. Med.*, **92**, 96–99 (1956); *Chem. Abstr.*, **50**, 13176*g*.

Survey of the Tannin Content of the Bark of *Pinus Radiata*. Experiments on the Countercurrent Extraction of *Pinus Radiata* Bark. P. J. Martin. *N. S. Wales Forrestry Comm., Div. Wood Technol., Rept. No. 4*, 5 pp. (1956); *Chem. Abstr.*, **50**, 13439*d*.

Vegetable Tanning Materials of the U. P. (United Provinces). R. K. Agarwal and G. D. Panda. *Tanner (India)*, **11**, No. 3, 13–16 (1956).—A shortage exists in the main tanning materials now used (babul bark and myrobalans). This article lists the tannin contents of 36 Indian plant species, summarizes the results of tanning tests that have been made with some of them, and discusses others that appear worth testing. H.B.M.

Changes In Fiber Structure of Hide during Manufacture of Chrome Side Upper Leather. M. Dempsey. *J. Soc. Leather Trades' Chemists*, **40**, 298–309 (1956).—Photomicrographs were used to examine dried and wet salted hides in the raw, limed, pickled, "blue", dyed and fatliquored, crusted, staked, and finished stages. Opening up of the hide is apparently continuous throughout the wet processes up to the fatliquored stage, and maximum opening up at the end of liming should not be the goal. Too little opening up of the hide in the limed stage in one tannery resulted in excessive staking, in which fiber bundles were broken, to soften the leather. On drying, chromed fibers restick, but after staking the structure is to a limited extent reopened. Toggle drying of leather lowers the angle of weave. Wet salted hides were less compact through the tannery processes than dry hides, and finished leather from the latter source was stiffer and stronger. J.M.C.

The Distribution of Ortho- and Para-cortical Cells in Wool and Mohair. R. D. B. Fraser and T. P. Macrae. *Textile Research J.*, **26**, 618–19 (1956).—Radially differentiated ortho-para distribution may be a fairly general feature of wools and wool-like keratin fibers with little or no crimp, the terms ortho and para being understood to indicate relative differences in the reactivity of individual cells toward basic dyes rather than a direct correlation with the ortho- and para-cells of fine crimped wool. This idea is attractive, but it may require modification and elaboration to include the spatial distribution of the two types of cells and the less pronounced contrasts in dye affinity found in kid mohair. R.M.L.

A Spectrophotometric Method for Determination of Cysteine and Related Compounds. Y. Avi-dor and J. Mager. *J. Biol. Chem.*, **222,** 249–58 (1956).—Reaction between thiols and fluorpyruvic acid produces a compound which exhibits a characteristic spectrum in the U. V. with a peak between 265 and 275 millimicrons. A spectrophotometric method suitable for determination of mercaptoethylamine, cysteine, homocysteine, and related compounds is described. J.M.C.

Evaluation of Test Methods by the Sensitivity Criterion. Anon. *Natl. Bureau of Standards Tech. News Bull.*, **40,** 139–40 (1956).—The sensitivity of a method, A, is defined as $(\triangle A/\triangle Q)/\sigma_A$, where A is the reading, Q is the property studied, and σ_A is the standard deviation. Two methods, A and B, may be compared by determining the ratio of their respective sensitivities, which is $(\triangle A/\triangle B)/(\sigma_A/\sigma_B)$. See Mandel and Stiehler, *J. Research Natl. Bureau of Standards*, **53,** 155 (1954). H.B.M.

Chemistry of the Process of Tanning of Gelatin. V. A. Veidenbakh. *Zhur. Priklad. Khim.*, **29,** 918–22 (1956); *Chem. Abstr.*, **50,** 14253*d* (1956).

Surface Film Studies of the Mechanism of Vegetable Tanning. A. F. Lanham and K. G. A. Pankhurst. *Trans. Faraday Soc.*, **52,** 521–28(1956); cf. *JALCA*, **51,** 565 (1956).—Surface pressure, potential, and viscosity measurements were made on collagen and N-methoxy methyl nylon monolayers spread on dilute solutions of wattle tannin and tannic acid. Both tannins were purified by adsorption on hide powder, washing with distilled water, and desorbing with 40% aqueous acetone. The characteristic change brought about by tanning a monolayer of collagen or N-methoxy methyl nylon is a considerable rise in surface viscosity. This is taken as evidence of cross-linked films. However, surface pressure and surface potential data also must be considered in interpreting results. Experiments using a water-soluble resorcinal-formaldehyde resin as tanning material gave results similar to those with the natural tannins. Since the surface potential is not invariably changed by the tanning reaction, and since tanning can occur between nonionic reactants, it is concluded that hydrogen bonds, probably between hydroxyl groups of the phenolic tannin and carbonyls of the peptide protein backbone, are predominantly involved, and that ionic reactions, if they occur, play a subsidiary role. J.M.C.

A Highly Alkaline pH Standard. *Leather Mfr.*, **73,** No. 9, 15 (1956).—The National Bureau of Standards recommends the adoption of $Ca(OH)_2$ as a new pH standard (pH 12.45 at 25°C.) The $Ca(OH)_2$ must not be contaminated with other soluble alkalies. This standard together with the other 5 standards recommended by the Bureau provides for accurate pH measurements over the pH range 1.68 to 12.45 at 25°C. J.J.

The Soaking of Dried Light Hides for Full-Chrome Side Leather. M. Dempsey. *J. Soc. Leather Trades' Chemists*, **40,** 287–97 (1956).—A scheme for soaking dried hides intended for chrome side leathers is drawn up in

detail. Hides were soaked successively in water, salt solution, and the latter plus sulfide. After the water treatment, hides were lightly drummed, turned over several times during the rest of soak, and green fleshed for liming. The resultant leather was judged satisfactory by two of the participating tanneries, too soft by two others, and a little more mellow than usual by the third tanner. This variation is related to the vigor of the processes subsequent to soaking in the different tanneries. Fiber structure of hides soaked both according to the suggested plan and in normal fashion was studied by photomicrographs. One tanner, after employing the suggested soak plan, halved his time of liming and produced a leather better than his usual production. J.M.C.

Some Relationships between Water Uptake of Pelt and Tannin Fixation. G. Cooper and R. B. Newton. *J. Soc. Leather Trades' Chemists*, **40,** 279–286 (1956).—Water uptake (weight increase) of dry pelt shavings was determined in the presence of various salt and acid concentrations and compared with the fixed tannin combined under similar conditions. Wattle tannin was employed for the study. For any given water uptake, irrespective of pH or salt concentration, there was found a corresponding degree of tannage. A series of experiments designed to study the effects of various cations showed that (1) a constant water uptake–degree of tanning relationship held for each system, although the relationship is different for different systems, (2) the valence of the cation had no effect on water uptake or tannin fixation, and (3) arrangement of the cations in order of tannin fixed at a given water uptake results in an order resembling the Hoffmeister series. Tannin fixation in systems containing strong acids is greater for a given water takeup than in weak acid systems. J.M.C.

The Formation and Removal of Collagen in the *Carrageenin Granuloma.* D. S. Jackson. *Biochem. J.*, **64,** 8 P, (1956).—Carrageenin injected subcutaneously into guinea pigs stimulates formation of connective tissue. The formation of 3 collagen fractions, viz., neutral-soluble collagen, acid-soluble collagen, and insoluble collagen, in this situation was studied. Labeled glycine was incorporated into the fractions. Maximum concentration of collagen is reached in 14 days, but the wet weight of tissue reaches a maximum in 9 days and falls rapidly thereafter. This decrease in net weight is accompanied by an increase in neutral-soluble and acid-soluble collagens. Labeled glycine is incorporated most rapidly into neutral-soluble collagen. Neutral-soluble collagen is said to be the true precursor of mature collagen, and acid-soluble collagen need not be an intermediate between neutral-soluble and insoluble collagens. J.M.C.

Mechanization of the Tanning Industry. A. Kuzmin. *Tanner (India)*, **11,** No. 3, 17–18, 21 (1956); reprinted in *Leather World*, **48,** No. 39, 55–57 (1956).—The author describes the mechanization thus far achieved in the Thaelmann Tannery in Moscow, U.S.S.R. This includes several types of conveyers, drum loaders, mechanical removal of fleshings and shavings, and a machine for spraying 4 successive finish coats onto black Cr leather with partial drying between coats. Under development is a worm conveyer machine for

continuous soaking and liming. This is a drum about 10 feet in diameter and 45 feet long, divided into 6 sections by a spiral partition. The batch (3 tons) is loaded into the first section. The drum is rocked periodically. At predetermined intervals the drum is given a half turn, which advances the batch to the next section. A second batch is loaded into the first section, and the process is repeated. The last section delivers the batch to a container which is moved to the unhairing machine by a crane. A 50% reduction in time required for soaking and liming, and complete elimination of handling are claimed. No information is given as to duration of the operation or materials used. H.B.M.

Tanning Materials. Anon. *Leather and Shoes*, **132,** No. 12, 12 (1956).—Edwin R. Lobaugh, Leather, Shoes, and Allied Products Division of the U. S. Department of Commerce states that, since the U. S. is almost entirely dependent upon foreign sources for vegetable tannin and also for Cr, the government has made an over-all study of the supply situation and has encouraged private research and development of replacement materials. The results of government and private endeavor are as follows: (1) Research is being conducted on a pilot-plant scale on canaigre root and Douglas fir bark as tanning agents. (2) Waste liquors from the sulfiting process in the manufacturing of paper have been used in conjunction with vegetable tannin. (3) Syntans have been developed and when used with vegetable tannin give fast and even penetration. A new syntan has been recently developed which is a replacement material for vegetable tannin. (4) Zv and W salts are the most likely domestic replacement materials for Cr. (5) Aldehyde condensation products have been used for tannage. J.J.

The Leather Industry—What is Ahead for Leather in the Automotive Industry. F. O'Flaherty, W. T. Roddy, and R. M. Lollar. *Leather Mfr.*, **73,** No. 9, 27 (1956).—It is estimated that one billion pounds of chemicals are used per year by the leather industry. The manufacture of leather for the automotive industry uses approximately 200 million pounds. Research is leading to new methods of tanning and finishing upholstery leather. The new finishes give greater color variety and new surface effects to the leather and promise to aid in the future styling of automobiles. Leather belts and use of leather on the instrument panels of automobiles could be safety features of the cars of the future. The new advances in tanning and finishing are consuming more varied chemicals in ever increasing quantity. J.J.

Recent Advances in the Use of Insecticides in Animal Health. J. Carmichael. *Chemistry and Industry*, 1078–80 (1956).—An address. H.B.M.

Formation of Fibrils from Extracts of Skin. D. R. Cooper and P. Johnson. *Biochem. et Biophys. Acta*, **20,** 411–12 (1956).—Fresh cowhide was extracted successively with NaCl and sodium phosphate. The extracts were treated with $(NH_4)_2SO_4$, the precipitates were dialyzed, re-extracted with citrate buffer, and the extract was again dialyzed. The NaCl extract yielded fibrils,

generally helical but sometimes smooth, about 110 microns wide, lacking the characteristic fine structure of collagen. The fibrils contained proline but not hydroxyproline. The phosphate extract yielded fibrils resembling the untwisted fibrils from the NaCl extract. H.B.M.

Studies of Enzymes for Leather Manufacture. I.—Factors Influencing the Formation of Proteolytic Enzymes in Certain Molds. S. M. Bose, S. C. Dhar, and B. M. Das. *Tanner (India)*, **11**, No. 2, 17–20; No. 3, 27–31 (1956).—Various factors were studied to determine the best growth conditions for producing proteolytic enzymes for bating. Preliminary tests were made with strains of *A. parasiticus*, *A. oryzae*, *A. flavus*, and *A. niger*, grown in a solution containing 1% Difco peptone and 4% glucose, for 1 to 10 days, at pH 5.5, and 33°C. The entire medium and mold growth were triturated with sand and water and centrifuged, and the clear supernatant liquor was collected. The residue was treated in the same manner 3 times more. The combined supernatants were assayed for proteolytic enzyme by colorimetric determination of tryptophane solubilized from egg albumin (Anson's method). *A. parasiticus* produced the most protease. Optimum incubation period was 6 days. This strain, incubated 6 days, was used in all subsequent tests. Production of protease was maximum at pH 6.0, and at 33°C. The age of the culture (2 to 8 days) used to inoculate the medium had no effect on protease yield. Production of protease was increased by aeration of the medium, but the depth of the medium had little effect. Sucrose as carbohydrate in the medium gave slightly better protease yields than dextrose or levulose; next came soluble starch; maltose and especially lactose gave very low yields. Best results were obtained when the medium contained 4% each of sucrose and peptone. A number of proteins, amino acids, and inorganic nitrogen compounds were substituted for peptone; none gave as good results. Additions of 15 inorganic salts to the medium increased the protease yield to a variable degree. Simultaneous addition of the most effective salts ($CaCl_2$ and K_2HPO_4, 0.1%; Na_2SO_4 and $MgCl_2$, 0.05%; $MnSO_4$ and $ZnCl_2$, 0.001%) increased the protease yield by over 25%. H.B.M.

The Native and Denatured States of Soluble Collagen. H. Boedtkar and P. Doty. *J. Amer. Chem. Soc.*, **78**, 4267 (1956).—By employing several physical methods it has been determined that the molecules of soluble collagen from ichthycol are rod-like in shape and have constants of this order: molecular weight, 345,000; length, 3000 Å; and diameter, 13.6 Å. Parent gelatin is obtained through denaturation of soluble collagen, and a method is described for accomplishing this and at the same time inhibiting reaggregation. The number average and weight average molecular weights of parent gelatin are shown to be 125,000 ± 10,000 and 138,000 ± 8000, respectively. The ratio of the molecular weight of soluble collagen to that of parent gelatin is found in separate experiments involving heating directly in the light-scattering cell to be 2.5 (± 0.15):1. The conclusion from the various data is that the molecule of soluble collagen is composed of three polypeptide strands running lengthwise, and that it does serve without serious modification as the structural element of collagen fibrils. This molecule has the additional characteristics of tropocollagen, a hypothetical particle suggested by Schmitt, Gross, and Highberger

as the common building unit of the three forms of collagen observed with the electron microscope. Suggestions are put forward as to the arrangement of the three chains in the molecule based upon the data obtained. H.R.W.

Research to Develop New Uses for Leather. Anon. *Leather World*, **48**, No. 36, 8 (1956).—Dr. Sam R. Hoover, Assistant Chief of the Eastern Utilization Branch of the United States Department of Agriculture (USDA) speaking before an Agriculture subcommittee of the U. S. Senate in support of a $100,000,000-a-year special research program, stated that USDA research is aimed at (1) chemical modification of hides to make leather or other hide products with new properties and thereby obtain greater diversity of use for hides, and (2) development of better, quicker, and cheaper methods of handling and tanning hides. Work in USDA laboratories and on a pilot scale have developed (1) a resin tannage which makes white leather that retains its color and shows reversible shrinkage in hot water, and (2), from animal fats, detergents and softeners for plastics. These softeners can be added to plastics to the extent of 35 to 40% to produce plastics of greater flexibility and light- and heat-resistance. Work in process which shows promise includes (1) enzyme removal of hair at the slaughterhouse, to enable packers to ship stable hides in the dry state free of hair, and (2) combining hide with a chemically modified starch to produce leather that wears better, is waterproof and yet permeable, and keeps its size and shape over a wide range of temperature and humidity. J.J.

A Photomicrographic Investigation of the Fatliquoring Process. D. K. Das, S. K. Mitra, and B. M. Das. *Bull. Central Leather Research Inst., Madras*, **2**, 402–11 (1956).—Chrome-tanned leather, neutralized and non-neutralized, was fatliquored with (*a*) sulfated castor oil, or (*b*) a blend of sulfated and raw castor oil, or (*c*) was oiled with raw castor oil. The amount of oil applied was varied from 1 to 4% in each case. Penetration of oil was assessed by examination of sections stained with Sudan IV or Nile Blue. Sections were cut before and after drying and were examined to determine changes in microstructure and thickness of the leather on drying. Oil penetration was complete for (*c*), except that penetration was irregular when 1% oil was applied. For (*a*) and (*b*), penetration from the flesh was always 3–5 times deeper than from the grain side. Penetration increased with amount of oil given; it was also greater for (*b*) than for (*a*), and for neutralized than non-neutralized leather. Leather that was not fatliquored lost 61% of its wet thickness on drying. For fatliquored leathers this decrease varied from 54 to 32%, and decreased with oil penetration (and amount of oil given). In the dried, non-fatliquored leather, the hair follicles and interfibrillary capillaries were completely collapsed, splitting of fibers was lost, the fibers were stuck together, and the angle of fiber weave was horizontal. In the fatliquored or oiled leathers, the follicles and capillaries were open, there was a general increase in fiber separation and splitting with increasing penetration of oil, and the angle of fiber weave varied from 22° to 60°, with a tendency to increase with increasing oil penetration. H.B.M.

Comparison of Ion-Exchange Techniques with the Electro-chromatographic Method as a Tool in Chromium Complex Analysis. Con-

siderations on the Debate Between Shuttleworth and Gustavson. A. Kawamura. *Bull Japan Assoc. Leather Technol.*, **1,** 24–36 (1955); *Chem. Abstr.*, **50,** 15111*e*.

A New Method of Analyzing Tannins. A. Y. Onikienko. *Vestnik Leningrad Univ.*, **11,** No. 6, *Ser. Geol. and Geograf.*, No. 1, 111–15 (1956); *Chem. Abstr.*, **50,** 15111*g*.

Utilization of Pentosans [e.g., Rice Hulls] in the Preparation of Chrome-Tanning Liquor. Y. Sato. *Bull. Japan Soc. Leather Technol.*, **1,** 106–8 (1956); *Chem. Abstr.*, **50,** 15112*c*.

Laboratory Scale Tanning with Vegetable Tanning Agents. Y. Sato. *Bull. Japan. Assoc. Leather Technol.*, **1,** 37–40 (1955); *Chem. Abstr.*, **50,** 15112*d*.

Organic Chelating Agents as Aids to Industry. A. Taylor. *Chemistry and Industry*, **1956,** 1131–35.—An address dealing with the structure, mode of action, and uses of sequestrating agents in various industries, including the leather industry. H.B.M.

Low-angle X-ray Diffraction Patterns of Collagen. S. G. Tomlin and C. R. Worthington. *Proc. Roy. Soc.* (London), **A235,** 189–201 (1956); *Chem. Abstr.*, **50,** 14308*e*.

Submicroscopic Structure of Collagen. I.—Periodic Structure of Collagen Fibrils. A. Bairati. *Scientia Med. Ital.* (English ed.), **4,** 560–613 (1956); *Chem. Abstr.*, **50,** 14819*h*.

Cylindrical Lattice Structure of Collagen. G. N. Ramachandran and V. Sasisekharan. *Arch. Biochem. and Biophys.*, **63,** 255–57 (1956); *Chem. Abstr.*, **50,** 14835*c*.

An Exact Paper Chromatographic Estimation of Amino Acid Constituents. H. Boser. *Hoppe-Seyler's Z. Physiol. Chem.*, **296,** 10–18 (1954); *Chem. Abstr.*, **50,** 14850*i*.

Chemical Composition of Raw Stock of Mammalian Skin. I.—Determination of Protein Fractions. Y. Sato. *Japan J. Zoötech. Soc.*, **26,** 183–89 (1955). **II.—Changes of Protein Composition by Curing and Preservation.** *Ibid.*, 193–95. **Chemical Composition of Various Mammalian Skins.** *Ibid.*, 207–9; *Chem. Abstr.*, **50,** 15109*f*.

A Study of Reticulin. S. K. Sarker, S. K. Mitra, and B. M. Das. *Bull. Central Leather Research Inst., Madras,* **2,** 367–71 (1956).—The literature on reticulin is reviewed (41 references). The effect of pretanning operations on reticulin was studied, using the staining technique of Mitra *et al.* (*Bull. Central Leather Research Inst., Madras,* **1,** No. 12). Reticulin is not affected by curing, normal liming, or bating, and can be seen in wet Cr-tanned leather but not after drying. Lime liquor containing 1% Na_2S attacks reticulin very slowly. Disintegration of the reticulin network is noticeable after 14 days, and no reticulin can be seen after 30 days. H.B.M.

Bleaching of Vegetable-tanned Leather and Factors Influencing the Final Color of Leather. A. Pou and J. Tomas. *Bol. Asoc. quim. espanola,* **45,** 238–45 (1956).—To obtain a uniform and light color, along with good yield and quality, (1) delime completely; (2) raise the tannage to an adequate pH; (3) use an appropriate mixture of extracts; (4) wash thoroughly; (5) select bleaching chemicals with care; and (6) control drying carefully. H.K.

Finishing Materials in the Shoe Industry. M. Paniker de Pelach. *Bol. Asoc. quim. espanola,* **44,** 218–27 (1956).—Various finishing materials are discussed, with special emphasis on their chemical and physical behavior. H.K.

Spectrophotometric Studies in Leather Research. IV.—Determination of Acid Content of Vegetable Tan Liquors. D. Ramaswamy, A. Nagasiromani, and Y. Nayudamma. *Bull. Central Leather Research Inst., Madras,* **2,** 351–59 (1956); cf. *JALCA,* **51,** 570 (1956).—Potentiometric titration of acids in tan liquors does not distinguish clearly between organic acids and phenolic groups. The end point is taken arbitrarily as pH 5.8, or sometimes 6.5. The differential absorption (D.A.) technique (reference cited) has been used to distinguish weak acids from phenols. When a tannin (e.g., avaram) that contains little or no organic acid is titrated with NaOH, the D.A. increases linearly from the outset due to immediate formation of Na phenates. For a tannin, such as myrobalans, that contains acids, there is no increase in D.A. until the stronger acids are neutralized; then the NaOH–D.A. curve rises in a succession of linear segments of increasing slope as acids of decreasing strengths are neutralized; after all acids are neutralized the curve rises steeply. The end point of acid titration is obtained by projecting this final portion of the curve to the NaOH-axis. Similar curves are obtained with chestnut, divi divi, and sumac extracts, and with avaram extract after adding a mixture of acids. When known amounts of organic acids were added to myrobalans, the amounts found by D.A. titration agreed with the amounts added within −2 to +4.5%, except in the case of citric acid, where only 2/3 of the amount added was found by titration. The acid contents of myrobalans, chestnut, divi divi, and sumac, as determined by D.A. titration agree better with the potentiometric titration to pH 5.8 than 6.5, but actually the pH of the end point varies from 5.65 to 6.1, depending on the extract. H.B.M.

Conductometry in Leather Research. I.—Application to Syntans. D. Ramaswamy and Y. Nayudamma. *Bull. Central Leather Research Inst., Madras,* **2,** 360–66 (1956).—Sulfuric acid and sulfonic acid (RSO_3H) cannot

be differentiated by potentiometric titration but can be by conductometric titration with NaOH. There is a slight but distinct change in slope of the descending branch of the NaOH–conductance curve at the end point of titration of H_2SO_4. In the presence of phenol, or weak acid, the conductance curve rises slowly after passing through the minimum corresponding to complete neutralization of the strong acids, and then rises rapidly. Free phenol (including OH groups of RSO_3H) can be determined from the conductance curve in the absence of weak acids, and vice versa, but if both phenol and weak acids are present, the curve is hard to interpret. Conductance curves, and percentages of H_2SO_4, RSO_3H, and total OH, are given for 4 commercial syntans. H.B.M.

Physical and Chemical Characteristics of Some Indian Leathers. II.—Indian Sole Leathers. B. M. Das, J. B. Rao, and Y. Nayudamma. *Bull. Central Leather Research Inst., Madras*, **2**, 389–96 (1956).—Chemical analyses and some physical test data are given for 12 samples of Indian pit-tanned buffalo sole leather, 1 bag-tanned leather, and 1 reputable British sole leather. The 12 Indian pit-tanned leathers differed a good deal among themselves. The British leather had the highest degree of tannage, density, tensile strength, and shrinkage temperature; it contained the most water solubles and showed the lowest water absorption, but it was also lowest in abrasion resistance. The bag-tanned leather had the lowest degree of tannage (only 35), lowest density, and highest water absorption; its abrasion resistance was good. H.B.M.

Spectrophotometric Studies in Leather Research. VI.—A Note on the [Supposed] Coordination of Formaldehyde with Chrome Complex. Y. Nayudamma and D. Ramaswamy. *Bull. Central Leather Research Inst., Madras*, **2**, 412–13 (1956).—Theis and Kleppinger (*JALCA*, **42**, 391 [1947]) suggested that the increased fixation of HCHO by leather pretanned with Cr might be due to coordination of HCHO with Cr. Addition of HCHO (1, 2, and 3 moles per mole Cr_2O_3) to salt-free, SO_2-reduced, 33% basic Cr sulfate had no effect on the absorption of the Cr solution in the range from 230 to 300 mμ. Thus spectroscopic evidence does not support the cordination hypothesis. H.B.M.

PATENTS

Tanning. Brit. Pat. 748,563. Chemische Fabrik Grunau Akt.-Ges. Apl. July 10, 1953. Furs or unhaired skins and hides are tanned with a liquor containing a compound of chromium, aluminium, iron, zirconium, titanium, or the rare earth metals (hereinafter referred to as mineral tanning agents) and (a) protein fatty acid condensation products, or (b) condensation products formed by the action of protein degradation products on high molecular weight carboxylic acid halides and/or high molecular weight sulphonic acid halides of the aliphatic or aliphatic-aromatic series, or (c) ethoxy derivatives of (a) or (b)

produced by ethoxylation of (a) or (b) or the proteins or protein degradation products from which they are derived. The proportion of the mineral tanning agent is usually greater than that of the organic agent. The degradation products may be derived from all kinds of protein material and are preferably such as to have about 3 to 10 peptide groups in the molecule. The tanning liquors may be made up by adding the condensation product in admixture with mineral tanning agents to a liquor which may or may not already contain mineral tanning agents. Such mixtures may be produced by the degradation of mineral, preferably aluminum- or chrome-tanned leather by means of aqueous solutions of strong acids, e.g. hydrochloric or sulphuric acids at elevated temperatures, or lime under pressure. The acid halides referred to are: halides of fatty acids such as oleic, palm kernel, stearic, linoleic or synthetically available fatty acids; resin and naphthenic acid chloride, and sulphonic acid halides, preferably having alkyl groups of 10 to 20 carbon atoms; their reaction with the degradation product takes place in known manner in the presence of an acid-binding agent, and ethoxylation may be performed at any stage in the production of the condensation product. Subordinate proportions (e.g. 5–10%) of salt- and acid-stable emulsifying agents, e.g. polyglycol ethers or polyglycol esters of high molecular weight alcohols or phenols, or carboxylic acids, respectively. One or more stuffing substances, e.g. mineral oils (spindle or paraffin oil), fatty oils (olive oil, rape oil, neat's-foot oil, train oil), fatty alcohols (oleyl alcohol) or lecithin, slightly sulphonated if desired may also be added, preferaby in emulsified form. In the examples: (1) a calf skin is pickled in a solution of salt and sulphuric acid, tanned with a solution of salt and a condensation product of lime-degraded chrome-tanned leather and soya fatty acid, which has been after-treated with ethylene oxide, into which is introduced basic chromic sulphate, and then progressively neutralized with sodium carbonate; (2) the tanning liquor of (1) is replaced by a mixture of salt, chromium oxide and neat's-foot, train and spindle oils in an aqueous condensation product of casein and palm kernel fatty acid, which has been aftertreated with ethylene oxide; (3) cowhide is treated with an aqueous mixture of chrome, a condensation product of casein and coconut oil fatty acid, dodecyl polyglycol ether and the oils in (2); (4) fur skins are steeped in aqueous salt/sulphuric acid, coated on the flesh side with a fat emulsion and hung up to dry. They are then dyed and coated on the flesh side with an aqueous mixture of salt, a lime-degraded chrome-leather waste/dodecyl benzene sulphonic acid condensation product treated with ethylene oxide, oleic acid polyglycol ester, spindle and neat's-foot oils, chrome alum and sodium carbonate, and after re-application if necessary gradually dried at moderate temperatures (other agents could replace some constituents of the mixture, e.g. the oleic acid polyglycol ester could be replaced by dodecyl pyridinium chloride and train oil or slightly sulphonated train oil could replace either of the oils mentioned); (5) conventionally pretreated skins are tanned with an aqueous mixture of potassium alum, a condensation product of lime-degraded chrome-leather waste and soya oil fatty acid chloride, oleyl alcohol polyglycol ether and neat's-foot oil; (6) unhaired skins are steeped in a liquid consisting mainly of milk of lime and also if desired sodium sulphide or an arsenic compound and then treated with an aqueous mixture of common salt and formic acid. They are then tanned in an aqueous liquor of common salt and sodium sulphate to which is added at intervals portions of a solution of zirconium oxychloride, a condensation product of lime-degraded chrome-

leather waste and arachidic acid, octylphenol polyglycol ether, and neat's-foot oil; (7) calf skin is pickled in a salt/sulphuric acid aqueous solution and then tanned with an aqueous mixture of common salt, chromium sulphate and a condensation product of lime-degraded chrome-leather waste and stearic acid, after-treated with ethylene oxide, further quantities of chromium sulphate being subsequently added, and the mixture progressively neutralized with carbonate solution; (8) the procedure of example 7 is used with a tanning agent consisting of an aqueous solution of common salt, chromium sulphate, and an emulsion comprising neat's-foot, train and spindle oils dispersed in an aqueous condensation product of hydrochloric acid-degraded chrome leather waste and soya fatty acid chloride; (9) fur skins are treated as in example 4, wherein the tanning liquor is replaced by an aqueous solution of common salt and a condensation product of sulphuric acid-degraded chrome- and alum-tanned leather waste and dodecyl benzene sulphonic acid chloride after-treated with ethylene oxide and the remaining components specified in example 4; (10) conventionally pre-treated lamb or goat skins are treated with a composition comprising potassium alum, oleyl alcohol polyglycol ether, sulphuric acid-degraded alum-tanned leather waste condensed with soya acid fatty chloride and neat's-foot oil.

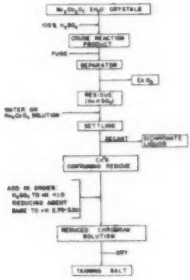
Tanning; Paper Containing Synthetic Resins. Brit. Pat. 747,183. Wolf & Co., J. Apl. March 3, 1953. Water-soluble products obtained by condensing dicyandiamide with formaldehyde in presence of boric acid (*see* Group IV (a)) are used for impregnating fibrous materials, e.g. felt, paper or leather. The material is then warmed to drain off water and cure the resin. Curing catalysts may be used if desired. The treatment is particularly suitable for leather, especially chrome-tanned leather but also leather tanned with alum, zirconium sulphate or other metal salt tanning agent. The leather is preferably treated with a surface active anionic sulphate or sulphonate, preferably in the form of its sodium or ammonium salt and with the dicyandiamide-aldehyde condensate in any order. Suitable anionic agents are naphthalene sulphonic acid-formaldehyde condensate; sulphonated phenol-formaldehyde condensate; sulphonated castor, teaseed or neatsfoot oil; sulphite lignin; or the sulphates of cetyl, lauryl or stearyl alcohol. In examples (2) chrome-tanned leather is split, shaved, washed, drained and treated with water at 43–49°C. A solution of the sodium salt of dinaphthyl methane disulphonic acid is added, the whole tumbled, washed at 60°C. and drained. Water is added at 60°C., followed by powdered dicyandiamide-formaldehyde condensate and tumbling.

Conventional fat liquoring follows. Examples 3 and 4 are similar. In example 6, one of the anionic agents mentioned above is added to sulphite wood pulp in the beater, followed by an aqueous solution of dicyandiamide-aldehyde resin and the treated films are formed into paper. Specification 736,955, [*Group* IV (a)], is referred to.

Process for Impregnating Leather and Product. U. S. Pat. 2,763,577. Paul F. Lawler, Dedham, Mass. No Drawing. Apl. Dec. 19, 1952. 1. Process of treating lightweight unfinished grain leather which comprises impregnating said leather from the grain surface inwardly with a liquid solution comprising synthetic, thermoplastic, water insoluble resin, a plasticizer for the resin and an

organic solvent for the resin and plasticizer, by applying said solution to the grain surface only of said leather, the proportion of plasticized resin in said solution being between 15% and 30% based on weight of plasticized resin to total volume of solution, proportions of plasticizer and solvent being sufficient to provide penetration of the solution into the leather to a depth not less than 15% of the average thickness of the leather and the amount of solution applied being between about 15% and 50% of the weight of the leather and sufficient to penetrate not less than 15% nor more than 50% of the average thickness of the leather.

Method of Obtaining a Chromium-containing Tanning Substance. U. S. Pat. 2,766,098. Tom S. Perrin, Painesville, Ohio, assignor to Diamond Alkali Company, Cleveland, Ohio, a corporation of Delaware. Apl. Nov. 19, 1952.

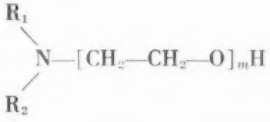


1. The method of obtaining a tanning substance from the waste bisulfate-containing residue from the manufacture of chromic acid by reacting bichromate crystals with sulfuric acid, which method includes the steps of slurrying said solid waste bisulfate-containing residue with an aqueous solvent for said bisulfate, said solvent being selected from the group consisting of water and a water solution of alkali metal hexavalent chromium salt, settling the resulting slurry to obtain a supernatant liquid and a solid-containing bottom, decanting the supernatant liquid, dissolving the solid-containing bottom, in sulfuric acid, the concentration and amount of said acid being sufficient to adjust the acidity of the resulting solution to a pH less than 1, adding to the resultant solution sufficient reducing agent to reduce the hexavalent chromium remaining in said solution to the trivalent state, adding to said solution sufficient alkali to provide a pH substantially within the range of 2.5–3.5, and removing water from the latter solution.

Tanning Leather. Brit. Pat. 748,995. Boehme Fettchemie Ges. Apl. Feb. 21, 1952. The invention comprises a process of tanning, wherein the tanning agent is a polyalkyl ether derivative of a high molecular organic sulphonamide which contains at least 6 carbon atoms in the hydrocarbon group. The sulphonamide can be used alone or in conjunction with other tanning agents, e.g. mineral, vegetable or synthetic tanning agents, e.g. alum, formalin, or fatty tanning agents, e.g. fish oil or fatty alcohol sulphonates. The tanning is preferably car-

ried out in aqueous solution at *p*H between 2 and 9, and the amount of agent fulled into the hides is preferably from 1—8 percent of the weight of dehaired hides. The process is applicable to animal hides and skins, e.g. of calf, sheep, goat, deer, roe or big-game hides, which have been prepared by soaking, liming and/or slackening, deliming, and if necessary by pickling. In examples: (1) delimed cowhides are fulled with dodecyl- or octadecyl-benzene sulphonamide, formic acid and then chromium oxide are added during the process, after which the leather is beaten, neutralized with sodium bicarbonate, rinsed, dyed and stuffed; (2) de-limed sheepskins are pre-tanned with formalin and soda, ammonium sulphate added, and the product tanned as in (1); (3) delimed deerskin is fulled with an emulsion of fish oil and aqueous dodecylbenzene sulphonamide, the hides stored for 4—8 days and excess fat washed out, leaving a chamois leather.

Process for Dyeing Leather with Acid and Direct Dyes. U. S. Pat. 2,763,528. Jules Meyer and Max Schwank, Basel, and Otto Albrecht, Neuewelt, near Basel, Switzerland, assignors to Ciba Limited, Basel, Switzerland, a Swiss firm. No Drawing. Apl. December 18, 1951. 2. A process for dyeing leather with a dyestuff selected from the group consisting of acid dyes and direct dyes, which leather has been tanned with a chromium salt, which comprises treating the leather at the latest during dyeing with a condensation product which in its free base state corresponds to the formula



where R_1 is a high molecular hydrocarbon radical selected from the group consisting of high molecular aliphatic hydrocarbon and high molecular alicyclic hydrocarbon radicals ,and R_2 is a member selected from the group consisting of hydrogen, lower alkyl and residues of the formula

$$—[CH_2CH_2—O]_nH$$

m and *n* being whole numbers, the sum $(m+n)$ having a value of at least 4.

Process for Tanning Skins. U. S. Pat. 2,767,043. Alexis E. Ushakoff, Beverly, Mass., assignor to Secotan Inc., Somerville, Mass., a corporation of Massachusetts. Apl. January 12, 1953. 1. In the method of tanning animal skins and the like wherein a water-wet skin is extracted of water by forcing an inert water-miscible organic solvent through the skin in an amount sufficient to extract and replace substantially all the water with the solvent, a mineral tanning agent is incorporated in the skin and the skin is finally dried of solvent with the mineral tanning agent neutralized therein: the improvement comprising contacting the skin with an aqueous solution of a mineral tanning agent to distribute the tanning agent throughout the skin before the water in the skin is extracted

and replaced with the organic solvent, thereafter supporting the skin upon and in conformity with a porous surface of a filter material having a porosity at least as fine as wool felt, and then forcing the organic solvent under a fluid pressure differential through the skin in the direction such that the solvent flows from the skin to the surface.

Manufacture of Leather. U. S. Pat. 2,768,056. Joseph S. Kirk, Newtown, Pa., assignor to General Dyestuff Corporation, New York, N. Y., a corporation of New York. Apl. December 28, 1951. 1. A process comprising impregnating hides and skins with a methyl vinyl ether-maleic anhydride copolymer in an aqueous medium maintained throughout the impregnation at a pH of about 2.5 to 4.0.

Vat Dyeing of Animal Fibers Using Esters. U. S. Pat. 2,768,051. William Kilby and James L. Harris, Lancaster, England, assignors to Standfast Dyers & Printers Limited. No Drawing. Apl. May 19, 1952. 1. A method of dyeing animal fibers in continuous fashion which comprises impregnating said fibers with a dyestuff selected from the group consisting of vat and sulphur dyestuffs, fixing said dyestuff upon said fibers by passing said fibers through an alkaline aqueous reducing liquor bath, removing the impregnated fibers containing entrained liquor from the bath and reacting with said entrained liquor at elevated temperature for a period of from 7 seconds to one minute an organic ester which is present and is being hydrolyzed by said alkaline reducing liquor to liberate acid to neutralize the alkali in the fibers, said organic ester being selected from the group consisting of ethyl lactate, normal propyl acetate, isopropyl acetate and diethyl tartrate while the liquor is fixing said dyestuff upon said fiber, at least the major amount of said neutralization occurring after the fibers are removed from the alkaline aqueous reducing liquor bath.

Tanning Agents. Brit. Pat. 745,774. Columbia-Southern Chemical Corporation. Apl. July 16, 1953. A tanning agent is prepared by forming an aqueous mixture of from one to four parts by weight of an alkali metal hydroxide and from one to twenty parts by weight of a carboniferous mineral such as peat or lignite which contains at least 10 per cent by weight of humic acid, the mix being digested for at least 15 minutes at 75° to 90° C. and then heated to dryness at from 150° to 350° C. The dry product is ground to a suitable size. Tannins such as quebracho extract and, in some cases, lime, may be added to the composition before drying.

Operating on Frozen Hides. Brit. Pat. 748,873. Bechtold, K. Apl. Nov. 12, 1952. Workpieces such as hides may be secured to a support by locating said workpiece thereon with a liquid such as water between the workpiece and the support, and freezing the liquid. In the illustrated apparatus, fur skins are placed successively on a rotating drum which constitutes the evaporator of a refrigerating plant. The skins pass in succession a roller brush, a plucking roller to remove projecting hairs, a clipping device consisting of a rotating cutter and a stationary cutter, and a strip cutter whereby the hair is shaved from the skins. Specification 572,367 is referred to.

Tanning Leather. Brit. Pat. 747,094. Farben-Fabriken Bayer Akt.-Ges. Apl. June 6, 1952. In a tanning process, there are employed as tannins amphoteric substances obtained by condensing more than one, preferably from one to ten, mols. polyvalent phenol with one mol. of a salt of ammonia or of a salt of an amine and with an aldehyde, the substances being used in the form of their water-soluble, acid-reacting salts, and the process is carried out so that the acidity of the tannin solution decreases towards the end of the tanning, the optimum *p*H, which has between 4.3 and 7 being obtained, if necessary, by treating the tanning solution with alkali or ammonia. The compounds used are suitably produced by the process of Specifications 747,092 and 747,093, [*both in Group* IV (a)], examples being condensation products of (i) resorcinol, ammonium chloride and formaldehyde, (ii) "brenzoel," aniline hydrochloride and formaldehyde ("brenzoel" being the residue obtained by the removal of monovalent phenols from phenolic oils extracted by solvents from the waste liquors from the low temperature carbonization of lignites &c.), (iii) "brenzoel," ethanoline and formaldehyde. The tanning process may be effected prior to or after (but not simultaneously with) tanning by other agents, e.g. vegetable, synthetic or chrome tannins, formaldehyde, paraffin sulphochlorides, fish oils, lignin sulphonic acids.

BOOK REVIEWS

Survey of the Production of Hides, Skins, and Rough-tanned Leathers in India, Pakistan, Ceylon, and Africa. G. W. Douglas. Egham, England: British Leather Manufacturers' Research Association, 1956. vii +78pp. Price: 7 *s* 6 *d*.—The author spent 5 months in India, Pakistan, and Ceylon, and 4 months in the Sudan, East Africa, South Africa, and Nigeria, collecting first-hand information for this pamphlet. The result is a full and systematic discussion of the skin and hide resources, hide defects and what is being done about them, and tanning methods in the several countries. H.B.M.

Commercial Waxes. A Symposium and Compilation. (2nd ed.), ed. H. Bennett, New York: Chemical Publishing Co., 1956. 688 pp. $15—The first edition of this work appeared in 1944, and was reviewed in *JALCA*, **40**, 328 (1945). The second edition is larger by about 100 pages; the scope and arrangement are unchanged. The book deals with "waxes" in the sense of solids having wax-like properties regardless of chemical constitution, and consists of a short Introduction and 7 very long chapters, as follows: 1. Natural Waxes; 2. Manufactured and Synthetic Waxes; 3. Physical Properties of Waxes and Wax Compositions; 4. Wax Technology; 5. Waxes in Industry; 6. Glossary, Special Tables, and Substitutes; 7. Wax Formulary. Some of the chapter titles are misleading. Thus, Chapter 3, Physical Properties, is devoted almost entirely to methods for varying some physical properties of practical importance by using wax blends. The physical properties of individual waxes are given mostly

in Chapters 1, 2, and 6. Chapter 4, Wax Technology, deals almost exclusively with testing and identification of waxes, although a few pages on coloring and emulsification are included. Chapter 5, Waxes in Industry, includes a 3-page discussion of leather finishes, which is almost the same, word for word, as that given in the first edition. The same chapter contains 3 pages on saponified shoe creams, apparently reprinted from a 22-year-old article in *The Manufacturing Chemist*. The last chapter, Wax Formulary, includes 10 pages of recipes under Leather and Furs, and a few more that are applicable to leather under Polishes and Waterproofing.

This book contains a vast amount of information, not too well organized, some of which will be valuable to leather chemists, but most of which will not.

H.B.M.

CORRECTION

In the November, 1956, issue, p. 597, the last paragraph of the text should read as follows:

"Results thus far show that a green-salted sample contains six times more non-protein-nitrogen than does a brine-cured sample and that no essential difference exists between the other fractions."

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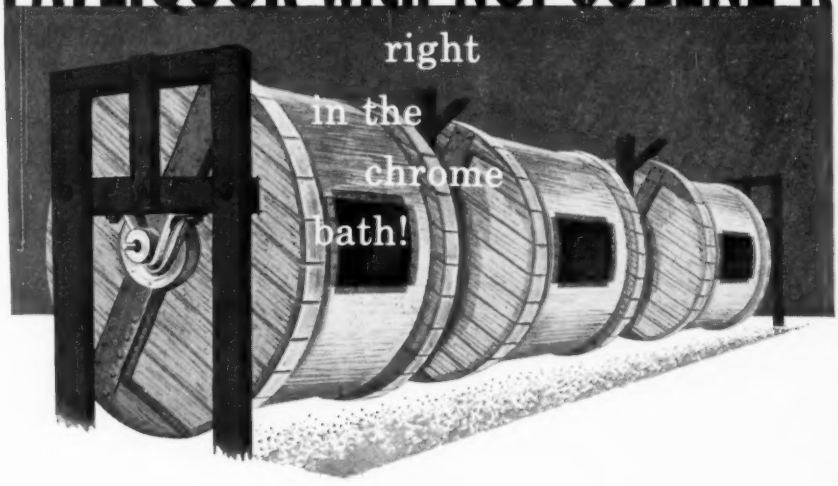

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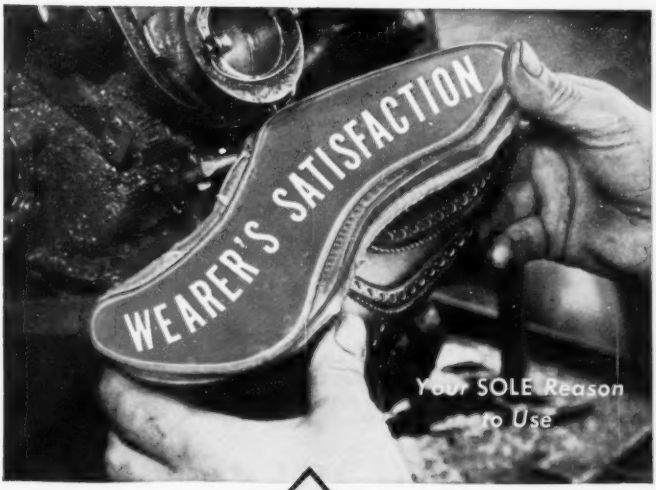

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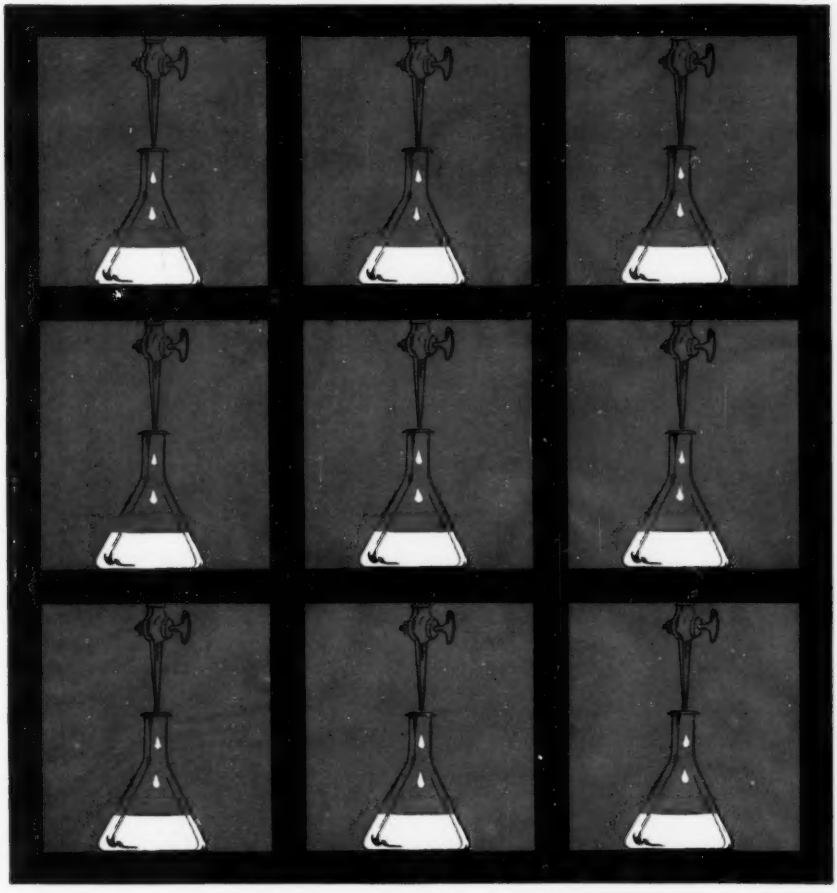

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